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THE

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AND

JOURNAL OF PHYSICAL SCIENCE.

WITH WHICH IS INCORPORATED THE "CHEMICAL GAZETTE."

A Journal of Practical Chemistry

IN ALL ITS APPLICATIONS TO

PHARMACY, ARTS, AND MANUFACTURES.

EDITED BY

SIR WILLIAM CROOKES, O.M., D.Sc., F.R.S., &c.

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THE CHEMICAL NEWS.

VOLUME CVII.

EDITED BY SIR WILLIAM CROOKES, O.M., D.Sc., F.R.S., &c.

No. 2771.—JANUARY 3, 1913.

TESTING METHODS OF RUBBER CONTENTS IN RAW AND VULCANISED RUBBER.

By W. A. DUCCA.

Two distinct chemical compounds of the rubber molecule have been the subject of extensive investigation during the last ten years, regarding a possible usefulness for a direct determination of caoutchouc in a given sample of raw or of manufactured rubber—the nitrosites or nitrosates as nitrogen compounds, and a compound with bromine as tetrabromide.

Harries deserves the credit of being the first one to make an attempt in the direction of a distinctly defined nitrogen compound. Almost simultaneously with C. O. Weber, he began a study of the action of nitrous acid gases upon solutions of rubber in benzole. Weber, who unfortunately did not live to finish his experiments, worked with nitrogen dioxide, developed by heating nitrate of lead. He obtained, or at least claimed to have obtained, an addition product of two molecules of NO_2 to one molecule of rubber of the formula $C_{10}H_{16}N_2O_4$ in a polymeric form. The compound would have to be classed as a nitrosate. Harries, on the other hand, applied N_2O_3, generated from nitric acid and arsenic trioxide. He stated that by varying the conditions he was able to separate three distinct compounds of a nitrosite character which he called nitrosites (*a*), (*b*), and (*c*).

It is not the purpose of this paper to enter into a detailed discussion of these well-known classical investigations, but the true composition of the compounds obtained in the reactions is of the utmost importance for the estimation of pure caoutchouc in a given sample of rubber. I therefore feel justified in giving a short review of the more important results reached by different authors and at different times.

Harries's three nitrosites are as follows :—

Nitrosite *a*, $C_{10}H_{16}N_2O_3$, is formed by a six-hour action of dry N_2O_3 upon a 1 per cent solution of rubber.

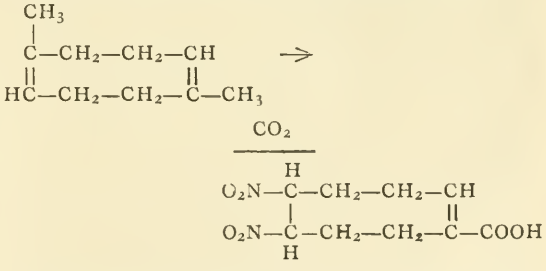
Nitrosite *b*, $C_{10}H_{15}N_3O_8$, is formed when dry N_2O_3 gas is passed from two to three days through a suspension of nitrosite *a* in benzole.

Nitrosite *c*, $C_{10}H_{15}N_3O_7$, is precipitated from a 1 per cent rubber solution in benzole by the action of wet N_2O_3 gases.

His first statements were later modified in some respects by Harries himself. The ultimate product of the action of N_2O_3 gas upon 1 per cent solutions of rubber in benzole was claimed to be uniformly nitrosite *c*, provided the reaction were allowed to go on for a sufficiently long time. Contrary to his first report, he gave as the best way to prepare this compound the use of N_2O_3 gas thoroughly dried over phosphorus pentoxide.

These results naturally induced Harries to apply the new compound for an analytical determination of caoutchouc. He obtained a satisfactory result on a sample of an uncured rubber compound, but did not make any attempts to develop the method any further, as this would hardly be within the scope of his work as a college professor and should rather be accomplished by a technical man. His work in this direction was taken up where he had left it by a number of investigators ; they practically all reached different conclusions based on various results.

The most exhaustive study of the subject was undertaken by Alexander with rather surprising results, not in accordance with Harries's observations. The action of N_2O_3 was shown to go much further than had been observed by either Weber or Harries. His method of precipitating the nitrosites from the rubber solution differed from Harries's method in so far as he generated nitrous acid anhydride from starch and 80 per cent nitric acid. The formula of the final product was given as $C_9H_{12}N_2O_6$, containing one carbon atom less than the original rubber molecule. This fact was explained by the oxidation of one of the two methyl groups of the caoutchouc molecule to carbonic acid gas, while the other one is supposedly oxidised only to the carboxyl group COOH.



That this explanation is possible from a theoretical standpoint is open to discussion. In support of his theory Alexander mentioned his observation of carbonic acid gas during the reaction. He certainly made a very thorough study of the matter, both theoretically and practically, and his analytical results are hardly to be doubted. On the other hand, Gottlob, who undertook a careful re-examination of Harries's experiments, comes to the conclusion that their results were correct beyond any doubt, and that he could confirm them in all respects. In his opinion, Alexander obtained different results only by not closely following Harries's method in every detail. We conclude

from these contradicting statements, that it is, to say the least, very difficult to obtain uniform results, a fact which is not surprising at all. Weber very justly pointed to the indefinite composition of nitrous acid gases. It seems perfectly natural that under such conditions indefinite reaction products will result. Furthermore, every chemist working with these nitrosites or nitrosates will experience the practical impossibility of determining their purity by the ordinary well-known tests. Ultimate analysis by combustion therefore does not yield reliable information as to their true composition; the figures obtained are likely to represent the mean percentages of carbon, hydrogen, and nitrogen in several distinct compounds. In accordance with my own experiences, I fully support Alexander's latest views:—The nitrosate method is not of real value, at least not at the present time, for the estimation of actual caoutchouc in either raw or vulcanised rubber. For the determination of the vulcanisation confficient it may prove to be an excellent method. Here it is not obligatory to know the exact composition and purity of the nitrosate, which is used only as a means to completely precipitate the sulphur of vulcanisation. Of course, this question cannot be considered as definitely settled, and it will require a long and careful study of all the conditions before it can be established as a well founded fact to hold true in any case and for any form of soft vulcanised goods.

The advantage of the method for the latter purpose consists chiefly in the elimination of the many troublesome fusions with the soda potassium carbonate and potassium nitrate mixture, especially unsatisfactory in presence of a large percentage of mineral matter. The precipitate can be finely powdered, and is therefore applicable for rapid sulphur determination by ignition with sodium peroxide, whereby the sulphur is oxidised to sulphuric acid in the form of sodium sulphate, which in turn can be precipitated as barium sulphate. The sample has naturally to be first extracted with acetone in the usual way to remove free sulphur; any vulcanised oils are separated by saponification. One-half grm. of the sample thus prepared is treated with 50 cc. of kerosene (boiling-point up to 300° C.) until completely dissolved. Mineral matter can be removed either before nitrosation by centrifuging the kerosene solution or afterwards by pouring it with the nitrosate on a filter, and dissolving the rubber compound in acetone, whereby the mineral matter is left on the filter. The acetone solution is either evaporated to dryness or poured into cold water to separate the nitrosate in a crystallised form. The latter method will secure a purer material, but necessitates an additional filtration. It is very essential to pour the acetone solution into water and not the water into the acetone, and to have the water cold, else the nitrosates will separate in an oily layer which does not crystallise very well, and is therefore hard to filter. The resulting yellow powder is mixed with sodium peroxide in suitable proportions and ignited in the usual way, as, for instance, in coal analysis for the determination of sulphur.

The tetrabromide method for the direct determination of caoutchouc was originated by Budde, and naturally received much more general attention on account of its less complicated nature and greater rapidity. Originally designed as a gravimetric method, it has undergone several changes, necessitated by the results of a number of investigators. But, even at the present time, it has not been developed to such a degree of accuracy as to deserve universal recognition, One fact stands out clearly:—All possible sources of error have been laid bare, so that the investigator when trying to apply the method for his special purposes can easily recognise all difficulties and obstacles he is liable to encounter. The investigations published in connection with this problem, finally leading up to the present status of the tetrabromide method, form a very interesting chapter in the history of the chemistry of indiarubber.

As stated before, Budde determined the rubber gravimetrically by first dissolving it in carbon tetrachloride, filtering the solution through glass-wool, and precipitating it from the filtrate with his bromination mixture (6 cc. of bromine and 1 grm. of iodine in 1 litre of carbon tetrachloride). After standing for twenty-four hours, one-half volume of alcohol was added, and it was allowed to stand until the precipitate had settled clearly. The supernatant liquid was poured through a weighed filter, the tetrabromide decanted with a mixture of carbon tetrachloride and alcohol, finally with alcohol alone in order to remove the excess of bromine. A number of serious objections were soon made to the method as proposed by Budde; several sources of error, influencing the results in opposite directions, were demonstrated. Fendler and Kuhn found during an exhaustive study of the solubility of rubber in various solvents that a considerable amount of rubber remains undissolved in tetrachloride; this would consequently be removed during the filtration required in Budde's method. While this fact would tend to render low results, other points are apt to increase the percentages found. It is next to impossible to wash the bromine out completely from the inner parts of the lumpy tetrabromide precipitate by mere decantation with carbon tetrachloride and alcohol. Protein and resin bromides, the solubility of which in alcohol and tetrachloride has been disputed, would also add to the weight of the precipitate; finally, claim was made by several investigators that bromine reacted with rubber not only additively but also by substitution, especially when allowed to remain a long time in contact with the rubber solution. Harries and Rimpel even claimed to have separated such a substitution product. Under the pressure of so many objections, Budde modified his method to a volumetric one. Instead of dissolving and filtering the solution in carbon tetrachloride he adds his bromination mixture to a mere swelling of the rubber in carbon tetrachloride, allowing it to react for but six hours. The precipitate is treated in the same way as before, and the wash-liquors poured through a filter to collect any possible particles of tetrabromide which might be carried off. The bulk of the precipitate is re-dissolved in carbon bisulphide, and separated from this solution with gasoline. This treatment has the double effect of removing the free bromine more exhaustively, and converting the precipitate into a stable crystallised form. The crystals are oxidised with nitric acid in the original vessel in which they were precipitated. A sufficient measured amount of standard silver nitrate solution is added, and the mixture gently heated. The nitric acid has to be replaced from time to time, and the manipulation continued until the bromine is all combined as silver bromide. The excess of silver nitrate is titrated back by Volhard's well-known method with ammonium thiocyanate. The formula $C_{10}H_{16}Br_4$ forms the basis for the calculation of pure rubber, four bromines corresponding to one caoutchouc, $C_{10}H_{16}$. In applying the method it is preferable to extract the sample first with acetone and eventually with alcoholic potash to remove completely the resins which might prove a disturbing factor by forming insoluble bromine compounds. Spence has only recently demonstrated by his investigations on rubber proteins and their behaviour towards bromine that the amount of the latter added to the tetrabromide in Budde's method is too small to materially influence the final results, provided the tetrabromide is calculated from the amount of bromine contained in the precipitate. The same author observed a regular loss of bromine when oxidising the tetrabromide with nitric acid as proposed by Budde, a fact which was confirmed by Hinrichsen and Kindscher. They therefore suggested to replace the oxidising and titrating process by a combustion in a current of oxygen or fusion with sodium potassium carbonate and potassium nitrate mixture. The fusion method has been improved and more fully described by Spence, who obtained satisfactory results. Budde's method therefore gives, in the case of raw rubber, even at its present stage, a fair idea as to the amount of rubber contained in a given sample. A more difficult problem faces the chemist in the case of vulcanised goods. The ques-

tion, "What reactions take place during the bromination?" becomes more complicated, and the composition of the products is a matter of great uncertainty; the method is therefore practically valueless for the estimation of pure rubber in cured goods.

Attempts to solve this problem were made by two different investigators. Axelrod precipitated the tetrabromide from a solution in kerosene with Budde's bromination mixture. The precipitate was washed in the same way as by Budde, and dried at from 50° to 60° C.; after weighing it was ignited and the ash deducted. By analysing a number of compounds of known composition he established a factor for the calculation of pure rubber from the bromo-sulpho compound. A moment's thought will at once reveal that such a determination is hardly applicable for general use. All sulphur of vulcanisation is included in the bromine precipitate, and, as the coefficient of vulcanisation is subject to considerable variation, it follows necessarily that the composition of the bromo-sulphur compound of rubber will be just as variable. We have, considering the present lack of a proper theory of vulcanisation, no means to judge what reactions take place and what compounds result when cured rubber is brominated. If the sulphur of vulcanisation is combined chemically with the rubber molecule, there is, of course, no room left for an addition of bromine to the double linkages which are saturated with sulphur. Huebener took this question into consideration, and, by adopting the Weber-Ditmar theory of vulcanisation, concluded the reaction product of bromine and vulcanised rubber consisted of three distinct compounds: tetrabromide, dibromomonosulphide, and disulphide. For purposes of calculation it is necessary to consider only tetrabromide and disulphide, because two molecules of dibromomonosulphide are equal to one molecule of tetrabromide and one molecule of disulphide. Therefore, not only bromine but also sulphur of vulcanisation has to be determined to find the equivalents for pure rubber. He proposed at the same time a somewhat simplified method originally designed for hard rubber, which has the advantage of eliminating the often very troublesome and long proposition of dissolving the rubber. The sample is finely rasped and brominated with elementary bromine under water. The results obtained in our laboratory have been invariably high, as it seems practically impossible to free the precipitate from the excess of bromine by a simple washing with hot water. Of course I have to admit that we have not made an exhaustive study of the subject, and therefore are not ready to condemn the method as valueless.

Even if all methods, as described before, have failed to be satisfactory to everybody and in every instance, their development marks a decided progress in rubber chemistry. It can be justly hoped that at a not too far distant time chemists will be able to submit such methods of analysis as will be acceptable to both the merchant and the manufacturer. The importance of this problem was recognised at the International Rubber Exhibition at London, when for the first time the International Testing Committee met in full session to discuss the questions which should be settled by this body.—*Journal of Industrial and Engineering Chemistry*, iv., No. 5.

Expulsion of Metals from Aqueous Solutions of their Salts by Hydrogen at a High Temperature and Pressure.—Wl. Ipatiew and B. Zrjagin.—When solutions of cobalt salts are subjected to the action of hydrogen at a high temperature and pressure, basic salts, metallic oxide, and finally the metal itself, are produced. The separation of the metal is an independent reaction taking place according to the equation $MX + H = M + HX$. Thus from cobalt sulphate solutions the basic salt of formula $CoSO_4.H_2O$ is formed, and metallic cobalt is deposited.—*Berichte*, xlv., No. 15.

ENAMELS FOR SHEET STEEL.

By ROBERT D. LANDRUM.

Enamels for sheet steel are boro-silicates of sodium, potassium, calcium, and aluminium and are, in every sense of the word, glasses. Such enamels are so compounded that they form a homogeneous, glossy coating on the surface of the sheet steel utensil, which will not be corroded by the acids or alkalis used in cooking and which will resist punishment both by impact and by rapid changes of temperature.

Although an enamel is a glass, the fact that it must adhere to steel and resist the abuse common to cooking utensils makes necessary the addition of other ingredients besides those used in manufacturing ordinary glass. In enamels, ground quartz, flint, or sand supply the silica, and felspar and clay the alumina. Fluorspar or calcite is added to supply the lime and cryolite to render the enamel translucent. Soda ash and pearl ash are fluxes adding sodium oxide or potassium oxide to the product, and borax furnishes the boric anhydride, which adds many desirable qualities, such as greater ductility and elasticity. Sodium or potassium nitrate is used in white enamels and manganese dioxide in dark coloured enamels as an oxidising agent. Oxide of cobalt is used in enamels which come directly in contact with the steel and adds adhesiveness to this coating.

For producing white enamels, oxide of tin is used; for blue, cobalt; for violet and brown, manganese; for grey, nickel; for green, copper or chromium; for yellow, uranium or titanium; and for red, iron, selenium, or gold.

Enamelling is still held as a secret art, and the formulas are carefully guarded. Most companies allow very few visitors to go through their plants and some keep their employees in ignorance by various schemes. In one American works, each of the enamel raw-materials is given a number. They are ordered, shipped, kept account of, and stored under their respective numbers, and only those in authority even know what materials are used. In this same factory employees of one department are not allowed in another, and after being employed in one department a man is barred from employment in any other. Some works have the formula for each enamel divided into two parts, one of which is mixed by one man, the other by a second, and certain proportions of each are then mixed together by a third man. In practically all enamelling works, the materials are weighed on a scale the beam of which is hidden from the labourers, who are also generally of foreign birth and are changed frequently.

The "Black Shape."—The sheet steel which is used for enamelled ware is as nearly as is possible free from carbon, silicon, sulphur, and phosphorus, and its manganese content is generally about 0·2 per cent. These sheets come in squares and oblongs from 27 to 20 gauge and are circled, stamped, and spun with as little heat treatment as possible and with the use of a lubricant that can easily be cleaned off. The ears, handles, and other trimmings are, as far as is practical, welded on, as rivetted joints are difficult to enamel.

Pickling Process.—The surfaces of the completed steel vessels are thoroughly freed from carbonaceous matter by annealing at a low red-heat and are then pickled in hot dilute acid, thoroughly rinsed in water, and then in weak alkali solution. After a quick drying they are ready to be enamelled.

The Enamel.—In the making of an enamel, the various raw materials are loaded from their respective bins into small cars called "dollies." These are filled to a line which approximates the correct weight, then they are pulled on a scale the beam of which is hidden from the workman, and the enamel-master indicates whether the load is light or heavy, and the workmen correct this by shovelling on more or taking some off. When each of the "dollies" is corrected so that the required amount of material for a mix is in it, all are dumped on a large, hard

maple floor, the coarser material on the bottom and the finer on the top. This pile is thoroughly mixed by shovelling, and is loaded into an electric elevator, which hoists it to its bin. There is a bin for each different kind of enamel, and a travelling bucket which holds a melt (abou 1200 lbs.) carries the mix to the tank furnaces where it is melted into a liquid glass.

These tank furnaces are regenerative, reverberatory furnaces like those used in the manufacture of glass, and natural gas or crude oil is an ideal fuel for them. However, in the older enamelling works, coal is used directly, and in the later ones producer-gas is used as a fuel. The temperature required for smelting the different enamels varies from 1000° C. for a glaze to 1300° C. for a ground coat, and, in most enamelling works, pyrometers are installed to assist in controlling these temperatures. Each furnace will give seven or eight melts in twenty-four hours.

After the enamel is melted into a liquid glass, a fire-clay plug in the front of the furnace is pulled out and the glowing liquid stream plunges out and is caught in a tank of cold running water. The reaction is terrific and the glass mass is torn and shredded, cracking into small pieces like popcorn, each of which is a myriad of microscopic seams and fissures. This "quenching," as the process is called, toughens the enamel and facilitates the process of grinding which comes next.

The water is drained from the tanks, leaving the "enamel frit." This is shovelled into pans (a certain weight to a pan) and is ready for grinding.

In the mill room, the enamel frit is ground in large ball mills for about thirty hours. These mills are cylindrical, about 5 feet long and 6 feet in diameter, and are lined with porcelain bricks. The frit is put into them with 50 per cent of water and several per cent of white ball-clay. For the white cover-coat enamels, tin oxide is also added. The mill revolves and the constant impact of the flint stones against the glass particles grinds them to an impalpable powder, which mixes with the water and the clay, forming a mass which has the consistency of rich cream. This is loaded into tanks, where it is allowed to age a week or so.

Application of the Enamel.—From the mill room the enamel is taken to the dipping room, where it is put into tanks that are like large dish-pans. These are sunk into tables, and at each tank a slusher works. The slusher takes the stamped-out steel vessel, which has been thoroughly cleaned, and plunges it into the enamel. When taken out, the wet enamel forms a thin film over the entire surface. By a gentle swinging motion, the excess of enamel is thrown off, and the vessel is placed bottom down on three metal points projecting from a board. Three or four vessels are put on a board; these are placed on racks and when the vessels are thoroughly dry they are carried to the furnace room.

The furnace room contains a long bank of muffle-furnaces, and in these the ware is put after drying. The temperature in these furnaces is about 1000° C., and here the little powdered particles of enamel are fused together in a solid glass coating over the vessel, the process requiring from three to five minutes.

Each coat is burned separately. For instance, we have a pudding pan that is to be a three-coat white inside, turquoise-blue mottle outside. It is first dipped in the ground coat enamel, the excess is shaken off, and the vessel put on a three-pointed rack and dried. After drying, the enamel stands in little grains all over the surface of the ware, adhering to the metal on account of the raw clay ground with it. At this stage every care must be taken, for a scraping, even of the finger nail, would take off some of the powdered particles of the enamel. This pan is then put into the muffle of the furnace, and the heat fuses all the little particles together, leaving a tight-holding vitreous coating all over the surface of the vessel. This fundamental coating is nearly black, due to the oxides of cobalt and nickel which it contains, and shines with a glass-like lustre.

After the vessel has cooled at the ordinary temperature of the room, it is again brought to the slushing room, and here is covered with an enamel—this time a white. It goes through the same process as before, except that a black bead is brushed around the rim. On account of the dark colour of the first coat showing through, this second coat, after it is burned, has a grey appearance, and is called the "grey coat" or "first white." The vessel is again sent to the slushing room, and is dipped into a white enamel, the excess shaken off, and before drying the blue-green enamel is sprayed on the outside.

This spraying process was at one time done by dipping a wire brush into the wet blue-green enamel and the slusher shaking it over the surface of the vessel, causing the blue enamel to fall in little speckles all over the white enamel. In most factories, however, spraying machines, which work on the principle of an atomiser, have been installed. A tank full of the coloured enamel stands over the table and the enamel is forced out through a nozzle in a spray by compressed air. The flowing of the enamel is controlled by the foot of the slusher as he holds the vessel in the spray. The vessel is then dried and the coating is fused in the muffle-furnace, the result being turquoise-blue spots on a white blackground.

The finished ware is assorted into three lots: firsts, seconds, and job lots. Some of the seconds and job lots are fit for re-dipping. They may have some little spots where the original vessel was not properly cleaned, and where, on account of the rust or dirt, the enamel did not adhere. These spots are filed or are held under a sand-blast until the exposed surface is perfectly clean, and then the vessel is covered with another coat of enamel.

There are schemes for saving money in all manufacturing plants, and in the enamelling business a large part of the profit comes from the residues. For instance, every bit of enamel is scraped from the tanks and tables, all sweepings from floors are saved, and all the waste water from the various departments is first carried into catch basins, and every few days these are cleaned and the residue, which has settled to the bottom, is taken out. The residues from all these sources are again melted with the proper amount of fluxing material and colouring matter, and this dark coloured enamel is used for coating the cheaper wares.

A German White Enamel.—In order to give an idea of the composition of a white cover-coat frit, such as is used on cooking utensils, and to show the method used by ceramists to calculate its so-called molecular formula, the following enamel, the formula of which is taken from the 1911 edition of the "Taschenbuch für Keramiker," p. 18, is used:—

Felspar 38·6 per cent, quartz 19 per cent, borax 15·4 per cent, cryolite 11·7 per cent, saltpetre 6·5 per cent, calcite 6·5 per cent, fluorspar 1·3 per cent, and magnesium carbonate 1·0 per cent.

Enamel Materials.—All the materials used were practically pure except the felspar, which was a pegmatite of the following composition:—

	Per cent.
Silica, SiO_2	70·66
Alumina, Al_2O_3	16·85
Potassium oxide, K_2O	5·93
Sodium oxide, Na_2O	4·61
Lime, CaO	0·52
Carbon dioxide, CO_2	0·41
Moisture, H_2O	1·02

This figures to a "molecular" formula of—

$$\left.\begin{matrix} 0{\cdot}45\ Na_2O \\ 0{\cdot}39\ K_2O \\ 0{\cdot}06\ CaO \end{matrix}\right\} Al_2O_3 \left\{\begin{matrix} 7{\cdot}11\ SiO_2 \\ 0{\cdot}34\ H_2O \\ 0{\cdot}06\ CO_2 \end{matrix}\right.$$

he molecular weight of which would be 602.

The Enamel.(*a*)

Batch mix. Material.	Per cent used.	M.W.	Mol. equiv.(*b*)	Na_2O.	K_2O.	CaO.	MgO.	Al_2O_3.	SiO_2.	B_2O_3.	F_2.
Felspar	38·6	602	0·0641	0·0288	0·0250	0·0038	—	0·0641	0·4558	—	—
Quartz	19·0	60	0·3167	—	—	—	—	—	0·3167	—	—
Borax	15·4	382	0·0403	0·0403	—	—	—	—	—	0·0806	—
Cryolite	11·7	420	0·0279	0·0837	—	—	—	0·0279	—	—	0·1674
Saltpetre	6·5	202	0·0322	—	0·0322	—	—	—	—	—	—
Calcite	6·5	100	0·0650	—	—	0·0650	—	—	—	—	—
Fluorspar	1·3	78	0·0167	—	—	0·0167	—	—	—	—	0·0167
Magnesium carbonate	1·0	84	0·0119	—	—	—	0·0119	—	—	—	—
	—	—	—	0·1528	0·0572	0·0855	0·0119	0·0920	0·7725	0·0806	0·1841

(*a*) A complete description of the manufacturing of this enamel, and of the physical properties of a ware coated with it, is given by the writer in "A Comparison of Ten White Enamels," in the *Trans. Am. Ceramic Soc.*, xiv.
(*b*) Molecular equivalent equals per cent used divided by M.W.

The other materials used were :—

Material.	Equivalent weight.
Quartz, SiO_2	60
Borax, $Na_2O{\cdot}2B_2O_3{\cdot}10H_2O$	382
Cryolite, $2Na_3AlF_6$, giving $3\,Na_2O{\cdot}Al_2O_3{\cdot}6F_2$	420
Saltpetre, $2K_2O{\cdot}N_2O_5$	202
Calcite, $CaO{\cdot}CO_2$	100
Fluorspar, CaF_2, giving $CaO{\cdot}F_2$	78
Magnesium carbonate, $MgO{\cdot}CO_2$	84
Felspar (given above)	602

The above total corresponds to the following molecular formula of enamel :—

$$\left.\begin{matrix}0{\cdot}497\ Na_2O\\0{\cdot}186\ K_2O\\0{\cdot}278\ CaO\\0{\cdot}039\ MgO\end{matrix}\right\}\ 0{\cdot}299\ Al_2O_3\ \left\{\begin{matrix}2{\cdot}513\ SiO_2\\0{\cdot}262\ B_2O_3\\0{\cdot}599\ F_2\end{matrix}\right.$$

—*Journal of Industrial and Engineering Chemistry*, iv., No. 8.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, November 21st, 1912.

Prof. Percy F. Frankland, LL.D., F.R.S., President, in the Chair.

The President referred to the loss sustained by the Society, through death on November 9th, of Prof. John William Mallet, LL.D., F.R.S., of the University of Virginia, who was elected a Fellow on December 15th, 1857, and an Honorary and Foreign Member on March 2nd, 1911.

Certificates were read for the first time in favour of Messrs. Neil Kensington Adam, 21, Barton Road, Cambridge ; Crellyn Colgrave Bissett, B.Sc., B.Met., 10, Claremont Place, Sheffield ; Daniel James Davies, B.Sc., 177, Le Marchant Road, St. John's, Newfoundland ; James Henry Edmondson, Newcroft, Urmston, Manchester ; Ulick Richardson Evans, The Kier, The Common, Wimbledon ; Alfred Leslie Howells, Bank Field, New Mill Road, Holmfirth ; Peter Thomas Leitch, care of John Edgar, Esq., 176, West George Street, Glasgow ; Thomas Joseph Nolan, M.Sc., 32, Newmarket, Dublin ; Cornelius Theodore Pollard, B.Sc., 21, Wharncliffe Road, Broomhall Park, Sheffield ; Siddons Siddons Wilson, 154, Burges Road, East Ham, E. ; Bertrand Turner, B.Sc., 55, Golden Hillock Road, Birmingham.

Certificates have been authorised by the Council for presentation to ballot under By-law I. (3) in favour of Messrs. James Crawford Douglas, Christmas Island, Straits Settlements ; Frederick Lyle Grützmacher, Technical College, Rockhampton, Queensland ; Max Hilbert, Hamburg, Germany ; Tanjore S. Natrajan, Bikshandarkoil P.O., Srirangam, Trichinopoly ; Carl Alfred Nowak, B.Sc., 2739, Mildred Avenue, Chicago, Ill., U.S.A.

Of the following papers, those marked * were read :—

*290. "*The Change in the Boiling-points of the Trioxide and Tetroxide of Nitrogen on Drying.*" By Herbert Brereton Baker and Muriel Baker.

As a result of a private communication from Prof. A. Smith as to the volatility of dried calomel, the authors found, on consulting their notehook containing the description of the experiments on the vapour density of dried nitrogen trioxide (*Trans.*, 1907, xci., 1862), two instances in which the liquid had failed to boil rapidly at 15°. A specimen of the liquid had fortunately been kept, which had been allowed to remain over phosphoric oxide for three years. This was sealed off in bulbs by immersing the whole in liquid air, and two of these were placed in tubes containing nitrogen, dried by contact with phosphoric oxide. After six months' keeping the bulbs were broken, and the boiling-point of the liquid at atmospheric pressure (757 mm.) was found to be 43°, instead of −2°, which is the boiling-point of the ordinary liquid. On cooling the tube to +10°, green drops formed at once, showing that undissociated nitrogen trioxide was present. When a small quantity of nitrogen, dried by passing through a long column of phosphoric oxide, was admitted to the apparatus, the very small quantity of moisture which it contained produced vigorous dissociation, and the expansion blew out the stopper. It has also been found that dried nitrogen tetroxide could be kept at a temperature of +69° without boiling. The ordinary boiling-point of this liquid is +22°. Further experiments on the boiling-points of dissociable substances are in progress.

*291. "*The Tendency of Atomic Weights to Approximate to Integral and Semi-integral Values.*" By Ernest Feilmann. (Will be inserted in a subsequent issue).

*292. "*The Constituents of Taraxacum Root.*" By Frederick Belding Power and Henry Browning, jun.

The material employed for this investigation consisted of the air-dried fresh roots of taraxacum (*Taraxacum officinale*, Wiggers). collected in the autumn from plants grown in England.

The root was found to contain an enzyme which slowly hydrolysed amygdalin, and an alcoholic extract of the root, when distilled with steam, yielded a small amount of a yellow essential oil.

From the portion of the alcoholic extract which was soluble in water the following compounds were isolated :—(i.) *p*-Hydroxyphenylacetic acid, $C_8H_8O_3$; (ii.) 3 : 4-dihydroxycinnamic acid, $C_9H_8O_4$; and (iii.) choline, $C_5H_{15}O_2N$. The aqueous liquid also contained a quantity of sugar, which apparently consisted chiefly of lævulose.

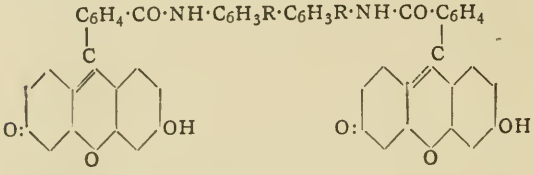
The portion of the alcoholic extract which was insoluble

in water consisted of a soft oily resin, amounting to 1·8 per cent of the weight of the root. From this material the following compounds were obtained :—(i.) Two new monohydric alcohols, *taraxasterol*, $C_{29}H_{47}\cdot OH$, and *homotaraxasterol*, $C_{25}H_{39}\cdot OH$, from which several derivatives were prepared ; (ii.) cluytianol, $C_{29}H_{46}O(OH)_4$; and (iii.) palmitic, cerotic, and melissic acids, together with a mixture of unsaturated acids consisting chiefly of oleic and linolic acids.

The so-called "taraxacin" and "taraxacerin" of earlier investigators are regarded as indefinite mixtures.

*293. "*Studies in the Diphenyl Series.* Part III. *Diphenyldiphthalamic Acids and Pyronine Colouring Matters containing the Diphenyl Group.*" By JOHN CANNELL CAIN and OSCAR LISLE BRADY.

Diphthalamic acids of benzidene, tolidine, and dianisidine are produced by the interaction of phthalic anhydride and the diamine at 100° in the presence of nitrobenzene. They condense with resorcinol in the presence of zinc chloride to give colouring matters of the formula—



(where R = H, Me, or OMe).

These colouring matters are also obtained by heating a mixture of (i.) the diamine, phthalic anhydride, and resorcinol with zinc chloride ; (ii.) fluorescein, the diamine, and the hydrochloride of the diamine ; and (iii.) the diphthalimino-derivative of the diamine with resorcinol and zinc chloride.

On bromination they yield octabromo-derivatives which can also be obtained by heating eosin with the diamine and the hydrochloride of the diamine.

The reaction appears to be a general one, as it takes place when di- and tetra-chlorophthalic or succinic anhydrides are used instead of phthalic anhydride, and when diethyl-*m*-aminophenol is substituted for resorcinol. Condensation takes place also with quinol, catechol, and pyrogallol, but in these cases the colouring matters produced are brown, and probably have a constitution different from the above.

DISCUSSION.

Dr. J. T. HEWITT drew attention to the interesting difference existing between the compound obtained by the authors and fluoresceinanilide. The latter was a colourless substance, and probably had a lactam constitution.

*294. "*Viscosity and Association.* Part III. *The Existence of Racemic Compounds in the Liquid State.*" By FERDINAND BERNARD THOLE.

The application of the viscometric method to the solution of the problem of the existence of racemic compounds in the liquid state has been extended to a much wider range of substances, both in solution and in the fused state.

The results obtained for viscosity and other physical properties have also been correlated.

In the present work the results obtained show that the majority of *dl*-liquids and solutions are merely conglomerates. Under this heading fall *ac*-tetrahydronaphthol, heptan-β-ol, octan-β-ol, carvoxime, octyl hydrogen phthalate, and ethyl mandelate.

On the other hand, distinct evidence of the existence of a liquid racemate has been found with dimethyl and diethyl racemates and *l*-menthyl *r*-mandelate. To these may be added the cases of racemic acid and perhaps *r*-mandelic acid previously investigated.

In the cases where racemate existence in solution has been substantiated dissociation is very considerable, and increases with increasing dilution of the solution.

The degree of dissociation at a given concentration and the rate of dissociation with dilution depend on the nature of the solute and the solvent, a condition which is paralleled by the ionic dissociation of salts dissolved in various solvents.

DISCUSSION.

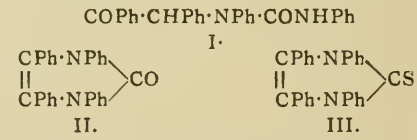
Mr. THOLE agreed with the President that tartaric acid and its esters were undoubtedly associated, and that the degree of association would be influenced by racemate formation.

This point had, in fact, been brought out in a previous communication on this subject.

In reply to Dr. McKenzie's question as to the identity of solutions prepared from racemic acid and from equal quantities of the enantiomorphs, the author stated that this point had been tested and the identity of the solutions established. The menthyl mandelates had been investigated, both in the fused state and in solution in amyl acetate. Although this liquid was one of the least dissociating solvents, dissociation of the racemic solute was very considerable, and probably in dissociating solvents such as alcohol or water dissociation would be practically complete.

295. "*Condensation of α-Keto-β-anilino-αβ-diphenylethane and its Homologues with Phenylcarbimide and with Phenylthiocarbimide.*" By SIDNEY ALBERT BRAZIER and HAMILTON MCCOMBIE.

α-Keto-β-anilino-αβ-diphenylethane and phenylcarbimide when heated together yield *desyl*-s-*diphenylcarbamide* (I.). This compound, on treatment with alcoholic hydrogen chloride, loses the elements of water, yielding 1 : 3 : 4 : 5-*tetraphenyl*-2 : 3-*dihydro*-2-*glyoxalone* (II.). The reaction has been extended also to the compounds in which aniline has been replaced by *o*-, *m*-, and *p*-toluidine, and by β-naphthylamine :—



The phenylcarbimide has also been replaced by phenylthiocarbimide, resulting in the production of 1 : 3 : 4 : 5-*tetraphenyl*-2 : 3-*dihydro*-2-*glyoxalthione* (III,) and its homologues.

The glyoxalones and the glyoxalthiones were found to be very stable substances, unaffected by acids, alkalis, or phosphorus pentachloride.

The glyoxalones yield salts with picric acid, but not with hydrochloric acid. These picrates can be divided into two classes, namely, (1) those formed by the aniline, *p*-toluidine, and β-naphthylamine compounds are red, and consist of 2 molecules of the base combined with 1 molecule of picric acid; and (2) those formed by the *o*- and *m*-toluidine compounds are yellow, and consist of the base and picric acid in equimolecular proportions.

296. "*Influence of the Sodium Salts of Organic Acids on the Rate of Hydrolysis by Alkali.*" By GEORGE SENTER and FRITZ BULLE.

The main results of the investigation are as follows :—

1. Sodium salts of organic acids, like the corresponding salts of inorganic acids, have only a slight effect on the rate of hydrolysis of ethyl acetate in alkaline solution.

2. Sodium salts of organic acids accelerate the hydrolysis of sodium bromoacetate by alkali to a still greater extent than do the salts of inorganic acids.

3. This effect has been traced, taking the case of sodium acetate as typical, to the intermediate formation of esters of sodium glycollate (for example, sodium acetylglycollate), which are hydrolysed by alkali as fast as they are formed.

4. From the extent to which the hydrolysis of ethyl acetate by alkali is retarded by monosodium salicylate, a provisional estimate of the second acid dissociation-constant of salicylic acid at 20° has been made.

297. "*Photo-kinetics of Sodium Hypochlorite Solutions.*" By William Cudmore McCullagh Lewis.

Aqueous solutions of sodium hypochlorite, both neutral and alkaline, are photochemically decomposed, the principal products of decomposition being sodium chloride and oxygen. This reaction cannot be brought about with measurable velocity by heat rays alone, the active region being the blue-violet end of the visible spectrum and the ultra-violet region. By means of suitably coloured filters it is possible to reduce the velocity of decomposition to zero. Since the photochemical decomposition is in the same direction as that followed, although very slowly, in the dark, the effect of the light is a catalytic one. The reaction proceeds completely after sufficient exposures, no measurable equilibrium point being obtained.

298. "*Constitution of Aconitine.*" (Preliminary Note). By Oscar Lisle Brady.

On treating aconitine with concentrated nitric acid a vigorous action takes place, and from the reaction mixture a compound can be obtained, which crystallises readily from alcohol and melts and decomposes at 200—205°.

This compound gives a strong nitroso-reaction; the solution in aqueous potassium hydroxide, on warming, becomes brown, and the substance cannot be re-precipitated with acids. By distillation with potassium hydroxide, dimethylamine was obtained. From the mother-liquor, after acidifying, acetic and benzoic acids were isolated, indicating that the benzoyl and acetyl groups of the aconitine remain in this compound. The substance is a carboxylic acid, and forms a silver salt; this is, however, unstable, and deflagrates on heating, and attempts to determine its molecular weight have given very discordant results. The following results were obtained on analysis: —C = 53·8; H = 5·5; N = 5·8; OMe = 12·4 per cent.

So far as can be judged, this compound is a simple benzenoid substance containing at least one methoxy and one carboxyl group, and the dimethylamino-, nitroso-, acetyl, and benzoyl groups.

An aqueous solution of chromic acid precipitates from an acid solution of aconitine an insoluble *dichromate*, $C_{34}H_{47}O_{11}N,H_2Cr_2O_7$. This substance on warming with dilute sulphuric acid gives a viscid mass, which was not further investigated. By the action of potassium permanganate in acid solution a crystalline substance is obtained, which is identical with that to which Carr (*Proc.*, xxviii., 253) has given the name oxonitin. The author's analytical results (Found, C = 59·5, 59·9; H = 6·4, 6·4; OMe = 18·2 per cent) and molecular weight determination by the ebullioscopic method in chloroform (431) agree well with the formula, $C_{23}H_{29}O_9N$, assigned to this substance; other properties, such as solubility and melting point, also agree.

The suggestion that the substance is a carboxylic acid seems unlikely in view that it is insoluble in cold alkalis; it seems probable that the compound is a ketone or an aldehyde, as there is some indication of the formation of a semicarbazone, but the preparation is rendered difficult owing to the insolubility of the compound. This substance has also been obtained in much better yield by the action of potassium permanganate in neutral solution.

From the mother-liquors after separation of oxonitin a crystalline *bromo*-compound was obtained melting above 300°. (Found, C = 40·9; H = 5·4 per cent).

299. "*Properties of Mixtures of Ethyl Alcohol, Carbon Tetrachloride, and Water.*" By Thomas Henry Hill.

Ethyl alcohol and carbon tetrachloride give a mixture boiling constantly at 65·2° and containing 16·05 per cent of the former component. The above three liquids also give a constant-boiling mixture, which distils at 61·8°, and has the following percentage composition as ascertained by the middle-point distillation method of S. Young:— Carbon tetrachloride, 86·3; alcohol, 10·3; water, 3·4.

300. "*Behaviour of Brass on Heating in Hydrogen at Temperatures below the Melting-point.*" By Ernest Alfred Lewis.

While making some experiments to ascertain if oxygen was an essential constituent of brass, the author noticed that on heating brass in pure dry hydrogen at a temperature of between 700° and 800° zinc volatilised to a large extent. In the preliminary experiments the brass was heated for one or two hours, and it lost under these conditions from 10 to 20 per cent of its weight. Further experiments were made, in which the brass was heated for three, six, nine, and twelve hours. It was found that the whole of the zinc could not be driven off even after twelve hours' heating, 3 or 4 per cent of zinc remaining behind.

The following result is typical of the experiments. 1·001 grm. of very pure brass containing 69·85 per cent of copper lost 0·272 grm. on heating for twelve hours, and the resulting metal contained 96·68 per cent of copper.

It was further found that if small quantities of tin were present in the brass it did not volatilise, but lead was found to be practically completely volatile. It was noticed that beautiful microscopical crystals of zinc formed in the cooler part of the tube, but the greater part of the zinc condensed as globules.

Another remarkable result of the experiments was that the metal, after heating, did not become brittle at all; in fact, a piece of sheet brass, heated in hydrogen until a large proportion of its zinc had volatilised, was found when cold to be quite soft and not in the least brittle like a cast and rolled copper sheet would become under the same treatment, due to loss of oxygen.

It may now be considered as proved that chemically combined oxygen is not an essential constituent of alloys of copper and zinc as it is of copper.

301. "*Inositol and some of its Isomerides.*" By Hugo Muller.

The author has continued his investigations on inositol and some of its isomerides, and showed that scyllitol, which was prepared from certain organs of plagiostomous fishes by Staedeler and Frerichs (*Journ. Prakt. Chem.*, 1858, lxxiii., 48), and quercine, obtained from acorns by Vincent and Delachanal (*Comptes Rendus*, 1887, civ., 1855), are identical with cocositol isolated by the author from cocos-palm leaves, and described in 1907 (*Trans.*, xci., 1767), and, as scyllitol was the first of these substances to be discovered, this name will be retained in future to represent them all.

The author described the action of solutions of hydrogen iodide and hydrogen chloride in acetic acid on inositol hexa-acetate, inositol, scyllitol hexa-acetate, and scyllitol, and showed that the action of hydrogen chloride gives rise to the formation of inositolchlorohydrin, $C_6H_6Cl(OH)_5$ (m. p. 185°); inositolchlorohydrin triacetate, $C_6H_6Cl(OH)_2(O{\cdot}CO{\cdot}CH_3)_3$ (m. p. 145°); and three isomeric modifications (α-, β-, and γ-) of inositolchlorohydrin penta-acetate, $C_6H_6Cl(O{\cdot}CO{\cdot}CH_3)_5$, which melt respectively at 247°, 110°, and 118°.

From the mother-liquors of the products of all the above-mentioned reactions two new isomerides of inositol were isolated, namely, iso*inositol*, which crystallises in large transparent crystals melting at 244°, and yields a crystallised *hexa-acetate* (m. p. 112°), and *ψ-inositol*, which is a microcrystalline substance, very soluble in water; the *acetate* is amorphous.

Scyllitol hexa-acetate, when heated with hydrogen bromide in glacial acetic acid, gave derivatives identical with those formerly obtained by the same reaction from inositol hexa-acetate.

302. "*Catalytic Decomposition of Nitrosotriacetonamine by Alkalis.*" By Douglas Arthur Clibbens and Francis Francis.

The discovery of a method whereby triacetonamine can be readily prepared in quantity has led to a re-investigation of the decomposition of the nitroso-derivative of this base by means of alkalis. It has been found that the nitroso-amine is catalytically decomposed by hydroxyl ions, giving nitrogen and a nearly quantitative yield of phorone. This

method is by far the easiest yet described for the preparation of this unsaturated ketone.

Experiments have been carried out in aqueous and aqueous-alcoholic solutions with varying concentrations of sodium hydroxide, the corresponding values of the constant for a unimolecnlar reaction being determined by measurements of the rate of evolution of nitrogen. This kinetic investigation of the reaction has shown that in all probability the decomposition, except over a range from about 0·05N- to 0·3N-NaOH, will afford a method for the quantitative determination of hydroxyl ions, comparable to that which Bredig and Fraenkel have found for hydrogen ions in the decomposition of diazoacetic ester.

303. "*Chlorides of the Mercurialkyl- and Mercurialkylaryl-ammonium Series, and their Constitution as based on Conductivity Measurements.*" By PRAFULLA CHANDRA RAY and NILRATAN DHAR.

The preparation of the following compounds was described:—(1) Mercurimethylammonium chloride, (2) mercuri*iso*butylammonium chloride, (3) mercuripiperazinium chloride, (4) mercuribenzylammonium chloride, (5) mercuribenzylmethylammonium chloride, (6) mercuribenzylethylammonium chloride, (7) mercuriethylenediammonium chloride, (8) mercuripyridinium chloride, (9) mercuripicolinium chloride, (10) mercurinicotinium chloride, (11) mercuripiperidinium chloride, and (12) mercurihexamethylenetetra-ammonium chloride. Although these salts are generally regarded as insoluble, they have been found to be sufficiently soluble to lend themselves to conductivity measurements. It is found that they all conform to the ammonium type of salts.

304. "*Position-isomerism and Optical Activity: Halogen Derivatives of Methyl Dibenzoyltartrate.*" By PERCY FARADAY FRANKLAND, SIDNEY RAYMOND CARTER, and ERNEST BRYAN ADAMS.

The preparation and properties of the dichloro-, dibromo-, and di-iodo-benzoyl derivatives of methyl tartrate were described. In each series the order of the rotatory power of the compounds, para>meta>dibenzoyl>ortho, is maintained. The rotations were determined in the fused state, and over a range of temperature from about 20° to 100°. The rotations as a whole diminish with rise of temperature, but the rotation of each of the ortho-compounds attains a maximum value below the melting-point, as already found by one of the authors in the case of ethyl dibenzoyl- and of ethyl and methyl di-*o*-toluoyl-tartrates. Incidentally, the *anhydrides* of *p*-chloro- and *m*- and *p*-iodobenzoic acids have been prepared.

305. "*Reactivity of the Halagens in Organic Compounds.* Part VII. *The Formation of Intermediate Compounds in the Hydrolysis of Sodium Bromoacetate.*" By GEORGE SENTER and THOMAS JOHN WARD.

The effect of sodium acetate and of sodium formate on the rate of hydrolysis of sodium bromoacetate has been measured, and the intermediate formation of sodium salts of glycollic esters has been proved by comparison of the results with those to be anticipated on the view that consecutive reactions take place during the hydrolysis.

The rate of hydrolysis of acetylglycollic acid and of sodium acetylglycollate in neutral and alkaline solution, and the influence of neutral salts on the rates of reaction have been measured.

Evidence was adduced to show that during the hydrolysis of sodium bromoacetate in fairly concentrated solution the reaction proceeds mainly by means of the intermediate formation and hydrolysis of sodium bromoacetylglycollate.

306. "*2-Phenyl-1:4:5:6-tetrahydropyrimidine and Benzoyl-αγ-diaminopropane.*" By GERALD EYRE KIRKWOOD BRANCH and ARTHUR WALSH TITHERLEY.

Numerous attempts to prepare benzoyl-αγ-diaminopropane, $NH_2\cdot[CH_2]_3\cdot NH\cdot COPh$, from αγ-diphthaliminopropane as starting-point proved unsuccessful. It is not possible to eliminate one phthalyl residue from this compound, or to rupture one of the rings, or to obtain the initially desired compound,—

$$C_6H_4{<}\begin{matrix}CO\\CO\end{matrix}{>}N\cdot[CH_2]_3\cdot NH\cdot CO\cdot C_6H_4\cdot CO_2H,$$

from the corresponding diphthalamic acid. The latter, moreover, even on cautious hydrolysis, suffers loss of both phthalyl residues.

Attempts on other lines to prepare benzoyl-αγ-diaminopropane were also unsuccessful; but its synthesis was finally effected from benzamidine and αγ-dibromopropane through 2-phenyl-1:4:5:6-tetrahydropyridine by the following steps:—

$CPh(:NH)\cdot NH_2 \xrightarrow{C_3H_6Br_2}$ Benzamidine

$CPh(:NH)\cdot NH\cdot[CH_2]_3\cdot Br,HBr \longrightarrow$ Tautomeric change

$CPh(:NH)\cdot NH\cdot[CH_2]_3\cdot Br \longrightarrow CPh{=}\begin{matrix}N\cdot[CH_2]_3\cdot Br\\NH_2\end{matrix} \longrightarrow$

$CPh{=}\begin{matrix}N\text{—}CH_2\\NH\cdot CH_2\end{matrix}{>}CH_2$ (2-Phenyl-1:4:5:6-tetrahydropyrimidine.) $\xrightarrow[\text{ammonia at 80°}]{\text{Dilute aqueous}}$

$NH_2\cdot[CH_2]_3\cdot NH\cdot COPh$ Benzoyl-αγ-diaminopropane.

2-Phenyl-1:4:5:6-tetrahydropyrimidine, which has previously been obtained in an impure form as an oil by Pinner (*Ber.*, 1893, xxvi., 2122) is a crystalline solid, melting at 72°, which is not very soluble in water. Its oxalate melts at 175°, and hydrogen oxalate at 180°. On benzoylation the base yields tribenzoyl-αγ-diaminopropane, $NBz_2\cdot[CH_2]_3\cdot NHBz$ (m. p. 144°).

Benzoyl-αγ-diaminopropane crystallises in transparent prisms melting at 46°. It is readily soluble in water, and its oxalate melts at 196°. On benzoylation it yields *s*-dibenzoyl-αγ-diaminopropane (m. p. 151°).

307. "*The Magnetic Rotation of Binary Mixtures.*" By FRÉDÉRIC SCHWERS.

In a binary mixture of liquids, between the changes of density C_v and of magnetic rotation C_r, there is a ratio Z (rotation constant), which possesses as a whole the same properties as the ratio A (refraction constant) between the changes of density and those of refractive power C_n. The common points are:—

1. For a given system, Z is independent of the concentration.
2. The value of Z diminishes with the decrease of wave-length.
3. The value of Z is characteristic for each system, and follows some general rules, as, for instance:—

(*a*) If we consider the mixtures of one liquid successively with the different terms of an organic series, Z decreases from the first term upwards.

(*b*) If we compare the solution of a liquid in water and in alcohol, we find a higher Z-value for the last-named solution.

(*c*) The values of Z in a carbon disulphide solution are much smaller (three to six times) than in the case of the corresponding aqueous solution; the mixtures with carbon disulphide are also particularly interesting, because they show that the general rules are the same, whether the mixture undergoes a dilatation or a contraction (aqueous mixtures).

4. In case the mixture undergoes electrolytic dissociation, Z increases with the dilution (=ionisation).

The difference consists in the fact that Z is always smaller than A. For the aqueous mixtures examined, Z has the average value of one-third of A; but this cannot be regarded as a general rule, as it is only one-sixth for carbon disulphide mixtures.

NOTICES OF BOOKS.

Elementary Chemical Theory and Calculations. By Joseph Knox, D.Sc. London: Gurney and Jackson. 1912.

This is a really admirable little book which should be in the hands of every student of elementary chemistry. It contains a short discussion of the essentials of chemical theory, with carefully graduated problems for solution. The chapters are usually short, and there are plenty of worked examples to drive each point home. The laws of chemical combination are stated clearly and explained in detail, and discussions of the atomic and molecular theories follow. Methods of determination of molecular and atomic weights are particularly well explained, and students should benefit greatly by having a clear conception of them. Calculations based upon equations are put at the end of the book, and students who have worked through the 200 problems which precede them should have no difficulty in dealing with them. A thorough grounding in elementary chemical theory is to be obtained from the book, which can confidently be recommended for use in the higher classes of schools and in colleges.

A College Text-Book of Quantitative Analysis. By Herbert Raymond Moody, S.B. (M.I.T.), A.M., Ph.D. (Columbia). New York: The Macmillan Company. 1912.

The author of this book believes that it is bad policy to allow the student who is beginning quantitative analysis to fall into pitfalls and make mistakes which lead to a great waste of time, and his special object has been to make his directions so clear and exact that even the beginner should be able to get quite accurate results in his first determinations. He certainly seems to have foreseen every possible cause of failure, and his lists of warnings and hints are copious. Throughout the book the experimental directions are annotated with explanations, printed in large type as footnotes, and there is very little excuse for the student to do unsuccessful work. He will be trained from the very first in accurate and careful habits, and if he is not allowed much freedom of thought and action, possibly quantitative analysis is to be regarded as a subject which does not aim so much at developing these characteristics as some other parts of his scientific work. The analyses described are comparatively few in number, but they include gravimetric, volumetric, and electrolytic processes. Of the latter only one method is described, but that is given in detail, while in the volumetric work the directions are particularly full and precise.

The Effect of the Labrador Current upon the Surface Temperature of the North Atlantic: and of the Latter upon Air Temperature and Pressure over the British Isles. By M. W. Campbell Hepworth, C.B., R.D. Geophysical Memoirs, No. I. Published by the Meteorological Office. 1912.

The author of this monograph has previously made a comparison of the changes in the strength of the Trade Winds of the Atlantic during each of the five years 1902-6, and of the changes in the Surface Temperature of the North Atlantic in the years 1903-7. From these comparisons it appeared that deviations from the average strength of the two Trade Winds during a series of months, or even during one month, were reflected in deviations from the normal in the average distribution of surface temperature in the North Atlantic in the corresponding series of months in the succeeding year.

For the purposes of comparison two zones were selected in the North Atlantic, the one lying between Florida Strait and Valencia and the other between that Strait and Cape Race, and the author has now shown that the encroachment of the Labrador Current is one of the most potent causes which tend to modify the influence of the Gulf Stream upon the temperature of the North Atlantic. Also the increased activity of the current in the five years from 1903-7, manifested by an increase of ice in the North-Western Atlantic, was generally followed by a diminution in temperature of the surface water in the Florida-Valencia zone. Moreover, a fall in sea-temperature is often associated with a corresponding fall in air-temperature at the Valencia, Sumburgh Head, and North Shields meteorological stations; and, in winter, with an increase of pressure. Also a rise in sea-temperature is accompanied by a rise in air-temperature, and, except in summer, with a diminution of pressure. The temperature of the sea is also lowered by the Labrador Current in another way. When the current encroaches upon the stream, where the two meet the course is diverted, and the stream flows north-eastward in a less northerly direction, so that the northern portion of the ocean is deprived of much of the warming influence of the stream from the south.

In the author's opinion air temperature over the British Isles is modified by changes in the surface temperature of the North Atlantic in three ways:—(1) By winds from the sea; (2) by the influence of sea temperature upon the paths of depressions that influence the wind and weather; (3) by a diminution of cloudiness. When the surface temperature of the north-eastern part of the North Atlantic is much below the average, atmospheric pressure over the Iceland-Faroe region has a tendency to increase, and centres of depression, passing over the British Isles, bring much cloudiness and rain. On the other hand, if the Gulf Stream is following its normal or a still more northerly course, the centres of Atlantic depressions pass to the westward or northward of these islands, and mild south-westerly types of weather or anticyclonic conditions prevail.

The diagrams from which these conclusions are drawn are reproduced in the monograph, which is an important contribution to our knowledge of the conditions which influence the effect of the Gulf Stream upon the temperature of the North Atlantic.

Treatment of Effluents from Dyehouses and Textile Factories. By J. H. Garner, B.Sc. Leeds and London: The Electric Press.

This book contains the prize essay to which the Silver Medal of the Society of Dyers and Colourists was awarded, and which was originally published in the Journal of the Society in the early months of the current year. The essay gave an outline, with diagrams and plans, of methods of treating the liquid refuse from the textile trades so that it may safely be allowed to flow into rivers and streams without deleterious effects, and also of processes of extracting valuable by-products; for example, from wool-washing refuse. The author was fortunate in being able to obtain access to many purification works, and to carry out analyses in the Laboratory of the West Riding of Yorkshire Rivers Board, and the essay, while not going into very great detail, gives a clear summary of some of the apparatus and methods used in purifying effluents.

Festschrift W. Nernst zu seinem Fünfundzwanzigjährigen Doktorjubiläum gewidmet von Seinen Schulern. ("Memoir Dedicated to W. Nernst by his Pupils in Celebration of the Twenty-fifth Jubilee of his Doctorate"). Halle-a.-S.: Wilhelm Knapp. 1912.

The papers composing this book have been contributed by a number of Prof. Nernst's pupils, whose activity in research is the best possible tribute to his inspiring teaching. They are written mostly in German, with a few exceptions in English or Italian, and deal with a wide range of subjects in physical and inorganic chemistry. It would perhaps be invidious to select for special mention any articles from so many of such excellence, and the book is a remarkable achievement from many points of view.

Untersuchungen über die Bidungsverhältnisse der ozeanischen Salzablagerungen ins besondere des Stassfurter Salzlagers. ("Researches on the Conditions of Formation of Oceanic Salt Deposits, especially the Stassfurth Deposit"). By J. H. van 't Hoff. Edited by Prof. Dr. H. Precht and Prof. Dr. Ernst Cohen. Leipzig: Akademische Verlagsgesellschaft. 1912.

This volume contains all the articles written by van 't Hoff, alone or in collaboration with other workers, on the subject of the formation of oceanic salt deposits. Most of the papers were originally published in the Reports of the Meetings of the Prussian Akademie der Wissenschaften. and physical chemists will find it a great convenience to be able to get them in book form. They are reprinted exactly as they were written, although the editors admit that van 't Hoff's style is often obscure and presents many difficulties to his readers. The original illustrations are reproduced, including those in two colours, which are collected at the end of the book. A memorial notice of van 't Hoff's life and work by Prof. Emil Fischer is also inserted.

OBITUARY.

HENRY DE MOSENTHAL.

Henry de Mosenthal was born in 1850 at Port Elizabeth, South Africa, and had been associated with Mr. Alfred Nobel, the inventor of dynamite, for some years before the formation in 1886 of the Nobel Dynamite Trust Company, Ltd., of which he was appointed technical secretary from the very first. This position he held until his death on December 17th last, from heart failure.

He was a well-known figure in the explosive industry of the world, and his business wisdom and great ability earned for him a high reputation in the business world and in the industry with which he was more specially connected.

De Mosenthal was a Fellow of the Institute of Chemistry for twenty years, and served for two periods of three years each as a member of the Council. He also belonged to the principal chemical and scientific societies, and will be remembered, not only on account of his connection with the manufacturing aspect of the explosives industry, but also for his valuable scientific work.

Most of his researches were contributed to the *Journal of the Society of Chemical Industry*, and among these may be mentioned the following:—"Treatment of Gold Ores at the Witwatersrand (Transvaal) Gold Fields," 1894, vol. xiii., p. 326; "The Life Work of Alfred Nobel," 1899, vol. xviii., p. 443; "Observations on Cotton and Nitrated Cotton," 1904, vol. xxiii., p. 292; 1907, vol. xxvi., p. 443; 1911, vol. xxx., p. 782.

The subject of Alfred Nobel was also treated in a biographical sketch in the *Nineteenth Century* of October, 1898, entitled "The Inventor of Dynamite," and, of course, De Mosenthal's intimate relations with Nobel enabled him to write a complete, and one might almost say classical, biography of Nobel's life and work.

De Mosenthal also contributed articles on "Nitro-Glycerin and Nitroglycerin Explosives" and on "Permitted Explosives" to the work published by the Explosives Section of the Seventh International Congress of Applied Chemistry, and entitled "The Rise and Progress of the British Explosives Industry" (Whittaker & Co., 1909).

De Mosenthal was an expert in microscopy and micro-photographic work, and, indeed, the earliest of his papers, that on the Treatment of Gold Ore, was already illustrated by micro-photographs. His technique, patience, and manipulative skill enabled him to obtain the most remarkable results.

His researches on Cotton and Nitrated Cotton were intended to obtain a picture of the constitution of the cellulose molecule, and he early recognised that the colloidal condition of the substances he examined necessitated methods other than were employed for bodies of a crystalline character. De Mosenthal accordingly determined values for a large number of the physical constants of cotton and of nitrated cotton, and these, together with his deductions, have thrown a great deal of light on this debated question.

In his first paper he was able to show the presence of stomata in the cotton fibre which had until then remained undetected. In his subsequent papers the effect of polarised light on nitrated fibres is described, and the connection between the degree of nitration and anisotropic effect criticised. The density of cotton and of nitrated cotton was determined, and an important difference was shown to exist between the increase in molecular volume with ascending degree of nitration in the case of cotton when compared with that afforded by the simpler alcoholic nitrates. The refractive index was investigated, films of the nitrated cellulose being employed, and from the values obtained the molecular refraction of the di- and tri-nitrates was calculated. The optical activity of nitrated cotton was examined, and its dextrorotatory character confirmed. Work on the dialysis of solutions of nitrocellulose in acetone ultimately established that the substance could not pass through a sound membrane, nor was it possible to detect any osmotic pressure.

In the last paper of the series De Mosenthal applied the results of his work to the nature of the constitution of cellulose, and stated his reasons for considering that it had an open chain structure. Whatever the view which will ultimately prevail as to whether this or a cyclic constitution is the more rational, the values of the constants determined by De Mosenthal, the description of his methods, and his impartial discussion of the results, constitute a material contribution to the advancement of our knowledge on this difficult subject.

De Mosenthal's papers were the result of much care and infinite thought. It is characteristic that on the day before his death he discussed his ideas and future programme of research with a friend, and it has been arranged that they shall form the subject of a scientific investigation by two of his friends and colleagues as a tribute to his memory.

As an illustration of his great versatility, it may be mentioned that, apart from his scientific work, De Mosenthal published several monographs of a popular nature on Explosives, in which he exhibited to a remarkable degree his talent for popular exposition of abstruse technical subjects and for making them understood by the general public. Some of these monographs appeared in the Savage Club Papers, of which Institution he was an esteemed member.

De Mosenthal was a bachelor and a remarkable linguist. He knew the four or five languages which he spoke with a thoroughness as though each was his own, and in addition he possessed the rare faculty of immediately grasping the vital point in a controversy. He was a trenchant, fearless, yet kindly critic, and he will be sorely missed by a wide circle of friends and colleagues whom it is no exaggeration to say he could count in every quarter of the globe.

JOHN W. MALLET, Ph.D., M.D., LL.D., F.R.S.

It is with much regret that we announce the recent death, at the University of Virginia, of Dr. J. W. Mallet, F.R.S., after a brief illness.

Born in 1832 in Ireland, John William Mallet early showed his aptitude for natural science, which was fostered and encouraged by his father, himself a distinguished engineer and scientific man. After his graduation as Bachelor of Arts at Trinity College, Dublin, in 1853, when he received a gold medal for Experimental Physics, he proceeded to Göttingen, where he devoted himself to the study of chemistry, having the good fortune to come

under the inspiring influence and the incomparable instruction of Wöhler. After receiving the degree of Doctor of Philosophy, he went to America, where he remained for the rest of his life, although he never became a naturalised American. He was appointed Chemist to the Geological Survey of Alabama in 1854, and subsequently became lecturer in chemistry at the University of Alabama, which post he resigned to place his services at the disposal of the Ordnance Department of the Confederate States. He took a prominent part in the control of the Arsenal and Ordnance Departments during the Civil War, and showed marked powers of organisation in strenuous and difficult positions. In 1865 he was called to the chair of chemistry at the University of Louisiana, which he vacated when he took a post as professor of industrial chemistry and director of laboratory studies at the University of Virginia. On the death, in 1871, of Dr. Maupin, the Professor of General Chemistry, he was appointed his successor, and this post he held with some breaks until his resignation in 1908. For family reasons he went to the University of Texas in 1883, returning to Virginia a year later and again leaving to take for a short time the professorship of Chemistry at the Jefferson Medical College in Philadelphia. He resumed his post as Professor of Chemistry at the University of Virginia in 1885, and although he resigned from the teaching staff in 1908 he continued to live at the University until his death.

Dr. Mallet's work as a teacher of Chemistry won him wide recognition in America. His most important publications include reports on the accurate determination of the atomic weight of aluminium and on water analysis. He was joint author with his father of the British Association Catalogue of Earthquakes.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clv., No. 19, November 4, 1912.

Forms in which Phosphorus and Calcium are present in Casein from Milk. L. Lindet.—When milk casein is precipitated by means of rennet it contains quantities of phosphorus and calcium which represent a phosphate intermediate between dicalcic and tricalcic phosphate. The author has found that half the phosphorus is present as phosphate of lime, while the other half is present as P_2O_5 in an organic compound. Three-fifths of the calcium saturates the phosphoric acid, and the rest saturates the free acid of the casein.

No. 20, November 11, 1912.

This number contains no chemical matter.

No. 21, November 18, 1912.

New Reagent for Free or Combined Chlorine or Bromine.—G. Denigès and L. Chelle.—To prepare the fuchsine reagent for detecting chlorine or bromine 10 cc. of a 0·1 per cent solution of fuchsine are added to 100 cc. of a 5 per cent (by volume) solution of sulphuric acid. The mixture gradually loses its colour, and in less than an hour it is ready for use. In the case of free chlorine or bromine a mixture is made of 25 cc. of this reagent, 25 cc. of acetic acid, and 1 cc. of sulphuric acid, and the liquid to be tested is added to 5 cc. of this mixture. A yellow colouration is produced with chlorine and reddish violet with bromine. For the combined halogens a mixture is made of 0·2 cc. of HCl, 1 cc. of concentrated H_2SO_4, 1 cc. of the fuchsine reagent, 5 cc. of the liquid to tested, and 1 cc. of chloroform. If the liquid contains 1 mgrm. of bromine per litre a violet colouration is produced.

Ether Salts derived ftom Cyclanols and Acids of the Formic Acid Series.—J. B. Senderens and Jean Aboulenc.—Using sulphuric acid as a catalyser the authors have prepared the ether salts resulting from the etherification, by acids of the formic acid series, of cyclohexanol, and *o*-, *m*-, and *p*-methylcyclohexanols. These ether salts are colourless liquids, which do not alter in air, except those of the ortho series, which slowly turn yellow. They have an agreeable smell, especially the formates and acetates. For the same alcohol the boiling-point rises 18·5 – 19° for each CH_2 group introduced in the acid; the formates are an exception to this rule. The densities diminish as one passes from the lower to the higher homologues of the acids, but not regularly. The indices of refraction in the ortho series are higher than those of the corresponding members of the meta series, while the indices of the meta and para series are about the same for ethers derived from a single acid.

Photolysis of Saccharose by Ultra-violet Rays.—Daniel Berthelot and Henri Gaudechon.—The authors' first experiments on the action of the ultra-violet rays on saccharose were carried out with relatively short wave-lengths, which rendered the liquids acid. Using slower ultra-violet radiations they have now found that the action takes place in two stages. Firstly, the saccharose is split up without liberation of gas, and secondly, gas is liberated. Thus the degradation of polyoses takes place in the same successive stages under the action of light as with ferments.

Transformation of an Alcohol into Sulphide or Peroxide by means of Sulphuretted Hydrogen or Hydrogen Peroxide.—R. Fosse.—When xanthydrol is treated with a liquid containing sulphide or hydrogen peroxide it behaves like a base, replacing two atoms of hydrogen by its own radical. Thus sulphide of xanthyl, $\left(O<\begin{matrix}C_6H_4\\C_6H_4\end{matrix}>CH\right)_2S$, or peroxide of xanthyl is formed. It is possible that the sulphydrate or hydroperoxide is formed as an intermediate product.

Complex Compounds of Platinous Chloride with Amino-acetal.—J. Tchougaeff and B. Orelkine.—When amino-acetal is added to a dilute solution of potassium chloroplatinite a yellow crystalline substance is deposited. Its formula is $Pt.2A—ACl_2$, where A represents the formula of amino-acetal. At the same time a colouriess compound of formula $Pt.4ACl_2$ is formed. When a solution of this chloride is precipitated with potassium chloroplatinite the salt $(Pt.4A)PtCl_4$ is obtained. Attempts to prepare two isomers of formula $(Pt.2A.2NH_3)Cl_2$ failed, and the isomerism described by Jörgensen does not seem to exist in this case.

Berichte der Deutschen Chemischen Gesellschaft. Vol. xlv., No. 14, 1912.

Anhydride of Bromacetic Acid.—Wilhelm Steinkopf.—When an equimolecular mixture of bromacetyl bromide and sodium bromacetate is distilled *in vacuo* a distillate is obtained, from which by repeated fractionation a fraction boiling at 133—135° under 12·5 mm. pressure can be prepared. When this fraction is allowed to stand it solidifies to a white crystalline mass, fusing at 41—42°. This substance is the anhydride of brom-acetic acid. It cannot be distilled under atmospheric pressure without undergoing decomposition. The anhydride can be prepared by distilling together bromacetyl bromide and sodium acetate under diminished pressure, but the yield is very poor, as is also the case when it is obtained by distilling *in vacuo* bromacetic acid with phosphorus pentoxide. It dissolves slowly in cold, but quickly in hot water, It rapidly volatilises in air; when allowed to stand even in the dark and in absence of air, it turns dark coloured. It has a piercing smell. It gives bromacetamide with ammonia, and bromacetic acid ethylene ester with glycyl.

No. 15, 1912.

Simultaneous Action of Catalysts.—Wl. Ipatiew.—Ordinary camphor when heated in presence of nickel oxide is converted into borneol at 320—358°, while borneol yields camphor when it is heated to 350—360° in presence of alumina. When camphor is heated in presence of both catalysts a reaction begins to occur at 200°, and the chief product is crystalline isocamphane. Borneol also yields isocamphane when heated to 220° with nickel oxide and aluminium oxide. To explain this action of the two catalysts the author assumes that a labile complex NiO,Al_2O_3 is formed, and readily decomposes, its components being thus separated in *statu nascendi*. Thus each component acts more energetically, and the reaction occurs at a much lower temperature, the result being the product of the complete reduction of camphor, isocamphane. In the reduction of camphor the primary catalyst is nickel oxide, while with borneol it is alumina.

New Gasometric Method of Estimating Nitric Oxide.—Oskar Baudisch and Gabriel Klinger.—When atmospheric air is led into nitric oxide which is in contact with solid potassium hydroxide, N_2O_3 is formed, and is immediately absorbed by the potash. The equations are $4NO + O_2 = 2N_2O_3$ and $2N_2O_3 + 4KOH = 4KNO_2 + 2H_2O$. Since four volumes of nitric oxide react with one of oxygen four-fifths of the contraction gives the volume of NO. The process is carried out in a Fuller's gas analysis apparatus. Some damp caustic potash is placed in a pipette, and all air is removed by means of mercury. The gas G is then introduced into the pipette, and then the air (L). The residual gas is then measured (V). The contraction K is given by $K = G + L - V$, and $K \times \frac{4}{5}$ is the volume of NO. This method is rapid and accurate, and it is immaterial whether N_2O or H are present.

The Philippine Journal of Science, Vol. vii., No. 2, 1912.

Action of Sunlight on Methyl Alcohol.—H. D. Gibbs.—When solutions of *p*-quinone in methyl alcohol are exposed to sunlight the principal products are formaldehyde and quinol. The oxidation of methyl alcohol to formaldehyde is catalysed by sunlight. Methyl alcohol is oxidised by hydrogen peroxide, the temperature being an important factor of the speed of the reaction. The chief product is formaldehyde. All evidence points to the conclusion that hydrogen peroxide is produced by the action of sunlight upon water and oxygen, both in the open air and in sealed tubes, and when water is present the formation of hydrogen peroxide will account for various sunlight oxidations.

Interference of Hydrogen Peroxide with the Milk Tests for Formaldehyde.—H. D. Gibbs.—The Hehner and Leach tests for formaldehyde in milk both depend upon the colour produced with milk proteids in the presence of iron salts and strong acids, the former with sulphuric and the latter with hydrochloric acid. The tests are very sensitive and the presence of 1 part of formaldehyde in 250,000 parts of milk can be detected by Leach's method. It, however, hydrogen peroxide is present, instead of the characteristic violet or purple colourations the colours obtained are yellow or brown. If the hydrogen peroxide is removed by a reducing agent a positive result can be obtained.

Memoirs of the College of Science and Engineering, Kyoto Imperial University. Vol. iii., No. 12, 1912.

Formation and Decomposition of the Quaternary Ammonium Bases and Salts.—Shigeru Komatsu.—The author has prepared many compounds of the general type N *a b c d* X, by the action of different alkyl iodides upon tertiary amines. In the preparation of the quaternary ammonium oxide, when allyl iodide or benzyl iodide was used, the mixture was cooled with cold water and the reaction was completed in twenty-four hours. When other alkyl iodides were used the mixture was heated on the water-bath for several hours. The use of methyl iodide was avoided as far as possible, for the methyl group has a tendency to expel the other groups combined with the nitrogen. The reaction product was washed with ether and acetone successively and then re-crystallised from hot alcohol, ethyl acetate, or water. Melting-point determinations gave results which frequently differed from those of other investigators. The quaternary hydroxides were prepared by treating the iodides with moist silver oxide and their decomposition by heat was studied. It was found that in the benzyl series the benzyl group is always given off. In the allyl series, when the compound contains two smaller radicles than allyl itself, the allyl is given off, but when one radicle is larger (excepting phenyl) and the other smaller than allyl, the smaller one is always given off. In other series of compounds the smallest group is never given off but remains attached to the nitrogen. In all cases one and the same ammonium hydroxide always yields the same tertiary amine.

MISCELLANEOUS.

Definition of "Fungi."—The United States Department of Agriculture have issued the following Amendment to the Rules and Regulations for carrying out the Provisions of the Insecticide Act of 1910:—"The term 'fungi,' as used in the Act and these regulations, is understood to mean all non-chlorophyll bearing plants of a lower order than mosses and liverworts (*i.e.*, non-chlorophyll bearing thallophytes), comprising rusts, smuts, mildews, moulds, yeasts, bacteria, &c."

Presentation to Otto N. Witt.—On March 31st, 1913, Prof. O. N. Witt will celebrate his sixtieth birthday. A token of recognition and remembrance is to be presented to him that day as an acknowledgment of his success as a teacher, his many sided activity as an investigator, his tireless promotion of chemical industry, his masterly command of language, both in speech and writing. The undersigned friends, colleagues, and pupils intend to offer him a plaque, executed by a master hand, and will be glad to receive subscriptions. Those who subscribe will receive a copy of the plaque in remembrance of the event. Subscriptions may be sent to Herr Dr. Frhr. C. v. Girsewald, Berlin-Halensee Karlsruher. Str. 29, or to the Commerz- und Discontobank, Depositenkasse KL, Berlin-Halensee, Kurfürstendamm 130, marked "Witt Testimonial."

New Materials for the Manufacture of Paper.—Experiments have been made with the following fibrous materials to investigate the possibility of their application for paper-making:—Papyrus from the Sudan and East Africa Protectorate, Spanish reed and Aristida from the Transvaal, "Nipa" fibre from the Federated Malay States, Borassus flabellifer leaves from Mozambique, bromelia leaves from Brazil. All these materials are capable of conversion into pulp suitable for the manufacture of paper, but as the raw materials would not realise more than about £3 per ton in the United Kingdom, it is unlikely that they could be profitably exported. Probably the best way to deal with these fibrous products would be either to convert the raw material into "half-stuff" and ship the latter, or to employ it locally for the manufacture of paper.—*Bulletin of the Imperial Institute*, x., 3.

MEETINGS FOR THE WEEK.

Monday, 6th.—Society of Chemical Industry, 8. "Estimation of Glyceryl Acetate in Essential Oils," by S. Godfrey Hall and A. J. Harvey. "Estimation of Moisture;" by F. H. Campbell. "Determination of Moisture in Foods, &c.," by W. P. Skertchly. "Determination of Water," by G. N. Huntly and J. H. Coste.

Tuesday, 7th. Thursday, 9th. Royal Institution, 3. (Christmas Lecture Epilogues, adapted to a juvenile auditory). "Meteorites—Frozen Worlds," by Sir James Dewar, F.R.S., &c.

THE CHEMICAL NEWS.

Vol. CVII., No. 2772.

LUSTRA CELLULOSE RESEARCHES.

By CLAYTON BEADLE and HENRY P. STEVENS.

I.—Hysteresis Curves produced by Testing Threads of Cellulose.

Our experiments have been conducted upon monofils precipitated from a solution of cellulose produced by the cuprammonium process, also upon multiple threads as are used for artificial silk. The curves have been obtained by means of the Schwartz machine (Prof. A. Schwartz, "The Testing of Rubber for Electrical Work," *Proc. Inst. Elect. Engineers*, 1910, Part 201, vol. xliv). In one case we took a monofil of 300 denier and applied to it a load up to 200 grms., and then decreased the load to zero in the manner as recommended by Schwartz and as adopted by us for the testing of rubber. The curve obtained is shown in Fig. 1. When the load has reached the maximum of 200 grms. the monofil had stretched to 7·26 per cent of its original length. On releasing the load it immediately recovered to point B; the distance from A to B may therefore be said to represent the "sub-permanent set" under these conditions.

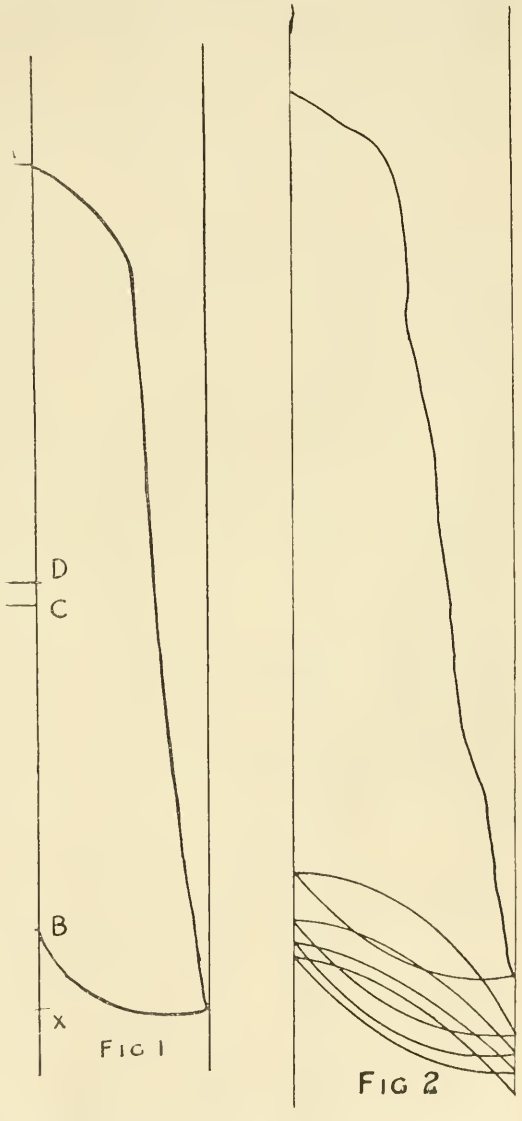
After allowing the above thread to remain without tension for a period of fifteen hours after the load had been released the thread had contracted to point C, and after a further period of four hours to point D. At this period of rest after tension the thread had recovered just one-half of the amount that it had stretched under load of 200 grms. The distance from A to X may be said to represent the elongation under a load of 200 grms., and from B to X its immediate recovery on release of load, and from D to X the amount of recovery after a period of nineteen hours. We did not determine what further recovery took place for more prolonged periods, but have reason to believe that the recovery continues for some considerable time.

In another case we took a multiple thread of 360 denier, consisting of 36 units and 100 twists per metre, and we applied to it a steadily increasing load up to a maximum of 350 grms. On reaching the maximum the load was released and again applied in the usual manner, and repeated four times. The results are shown in Fig. 2. The hysteresis loops so produced are not unlike those obtained with rubber and other substances. These loops clearly indicate the nature of the stretch, and its recovery and the fatigue as the result of repeatedly applying and releasing a constant load. As with rubber, the increments of extension obtained on subjecting the specimen to a series of cycles of extension and retraction with a given maximum load, appear to follow logarithmic law with respect to the number of the cycles.

In neither of these cases above cited did we apply a load approaching the tensile limit. Tensile strength determinations gave for the monofil and multiple thread a specific strength of 1·2 to 1·4 grms. per denier, and an elongation at break of 22 per cent for the monofil and 16 per cent for the multiple thread. We find that the results are very little affected by untwisting the multiple thread previous to testing. The hysteresis tests have been repeated on both kinds of cellulose threads with very similar results to the foregoing.

II.—Influence of Denier upon Breaking Strain and Elasticity of Monofils.

Before approaching the above subject we think it would be advantageous to give figures which, as far as we know, have never been published, showing the relationship between denier, cross sectional area in sq. mm., and diameter in millimetres. Perhaps the more usual way of expressing denier is on the assumption that one denier is equal to 0·05 grm. per skein of 500 yards or 450 metres. This is the denier on which we have more usually calculated, and which is largely adopted by the manufacturers and users of artificial silk both here and on the Continent. But we prefer the more scientific unit as employed by Dreaper and Davis, in which one denier is equal to 0·1 grm. per skein of 1000 metres or 10,000 metres length of yarn weighing



1 grm. (Dreaper and Davis, *Journ. Soc. Chem. Ind.*, Feb., 1912, xxxi., No. 4). This is a more scientific basis and more easily remembered and calculated.

Table I., which we have calculated for the purpose of this communication, shows the relationship of the denier, the cross sectional area and diameter for each denier between 1 and 20, and for every 10 denier between 20 and 400. We give it for each denier between 1 and 20 because, in the case of the finest multiple threads (artificial silk), particularly those such as described by Dreaper and Davis (*loc. cit*), which consist of 45 filaments in deniers

varying from 19 to 160, each individual filament will vary from about 0·5 to 3·5 deniers respectively. With ordinary artificial silk of, say, 100 denier and upwards, the number of filaments chosen is such that each filament has, roughly speaking, a denier of 10 or thereabouts. This is the ordinary commercial product, the average denier of the multiple thread of which may be put at 150, and the number of threads at 15.

Table I.

Denier.	Cross-sectional area sq. mm.	Diameter in mm.	Denier.	Cross-sectional area sq. mm.	Diameter in mm.
1.	0·00006	0·0092	120.	0·0080	0·1008
2.	0·00013	0·0130	130.	0·0086	0·1052
3.	0·00020	0·0160	140.	0·0093	0·1090
4.	0·00026	0·0184	150.	0·0100	0·1128
5.	0·00033	0·0206	160.	0·0106	0·1168
6.	0·00040	0·0226	170.	0·0113	0·1202
7.	0·00046	0·0244	180.	0·0120	0·1236
8.	0·00053	0·0260	190.	0·0126	0·1270
9.	0·00060	0·0276	200.	0·0133	0·1304
10.	0·00066	0·0292	210.	0·0140	0·1336
11.	0·00073	0·0306	220.	0·0146	0·1368
12.	0·00080	0·0320	230.	0·0153	0·1398
13.	0·00086	0·0332	240.	0·0160	0·1428
14.	0·00093	0·0344	250.	0·0166	0·1458
15.	0·00100	0·0357	260.	0·0173	0·1486
16.	0·00106	0·0368	270.	0·0180	0·1514
17.	0·00113	0·0380	280.	0·0186	0·1542
18.	0·00120	0·0390	290.	0·0193	0·1571
19.	0·00126	0·0402	300.	0·0200	0·1597
20.	0·00133	0·0412	310.	0·0206	0·1623
30.	0·0020	0·0504	320.	0·0213	0·1650
40.	0·0026	0·0584	330.	0·0220	0·1674
50.	0·0033	0·0652	340.	0·0226	0·1700
60.	0·0040	0·0714	350.	0·0233	0·1724
70.	0·0046	0·0792	360.	0·0240	0·1750
80.	0·0053	0·0825	370.	0·0246	0·1773
90.	0·0060	0·0874	380.	0·0253	0·1797
100.	0·0066	0·0921	390.	0·0260	0·1820
110.	0·0073	0·0966	400.	0·0266	0·1843

The diameter in the above table is given on the assumption that the threads are perfectly cylindrical, whereas this is seldom the case, more particularly in the ase of artificial silk, consisting of a number of filaments twisted together. The tendency in the case of artificial silk is to the production of threads which are hexagonal in section. The sections become angular in consequence of the pressure exerted by one thread upon the other. Similar sections are to be noted in many of the natural fibres from a similar cause. The resemblance to the hexagonal section is determined by the extent to which the fibres press upon one another in all directions. There is a greater tendency towards this hexagonal section in the case of multiple threads produced with rotating nozzles in the coagulating bath. This angularity of the cross section does not detract from, in fact it may rather add to, the sheen and lustre of the product.

Dreaper and Davis, in the above cited communication, show that when fine threads (in the form of multiple threads), varying between 0·492 and 3·56 denier, are tested for breaking strain, the breaking strain per denier is greater as the denier becomes less. Which, being put in another way, comes to this—that, within the limits above cited, the strength per unit of cross-sectional area increases as the diameter of the thread diminishes. This is attributed to a solid skin produced upon the surface of the thread, which skin is more or less of a uniform thickness irrespective of the diameter of the thread. Consequently, the proportion of the thick skin bears a much greater relationship to the total cross-sectional area in the smaller than in the larger threads, and it can only be in the case of small denier that the influence of the thick skin, in regard to the increase of strength and so forth, can make itself apparent. From this one is forced to the conclusion that, with ordinary commercial artificial silk, the influence of the "solid skin," as it is called, upon the strength of the product is almost infinitesimal. At any rate, its influence is so small as to be altogether masked by the other various factors which go to determine the physical qualities of the product.

In order to determine whether there could be discovered any relationship between the denier, percentage stretch at break, and the breaking strain, a number of monofils varying between 400 and 330 were produced in a factory under our own supervision, but entirely according to the commercial practice, and the finished skeins were tested by us with the results as given in Table II., which also gives in the last column the breaking strain in grms. per denier.

Table II.

	Denier.	Percentage stretch at break.	Breaking strain of thread, in grms.	Breaking strain in grms. per denier.
		Manufactured February, 1911.		
	400	21·2	565	1·41
	390	25·0	521	1·33
	380	21·0	563	1·48
	370	25·0	494	1·34
	360	21·0	481	1·33
	350	22·0	488	1·40
	340	22·8	471	1·39
	330	20·0	463	1·40
Mean	365	22·2	506	1·38
		Manufactured September 10, 1912.		
	280	23·3	467	1·38
	260	20·4	429	1·34
	250	25·0	415	1·34
	230	24·8	313	1·36
	210	26·7	294	1·40
	190	24·3	255	1·34
Mean	237	24·1	362	1·36

These monofils were made in February, 1911. As we wanted to extend the series we arranged with the factory to send us lower denier down to 190. These we tested in a similar way. It will be observed that the average grms. per denier of the threads made in September, 1912, was 1·36 (varying in deniers between 280 and 190), and

those produced by us in February, 1911, of the higher denier gave an average of 1·38. The average specific breaking strain is practically identical in the two sets.

It will here be noticed that the breaking strain in grms. per denier is remarkably constant, being in the neighbourhood of 1·40, and that therefore within the limits above recorded there cannot be said to be any influence as the result of variation in denier. The stretch at break shows a greater variation than the specific strength, but these variations do not appear in any way to be fixed or influenced by the denier. As will hereafter be shown, there are many factors which have a marked effect upon the specific strength and elasticity of artificial silk and monofils, and these are more than likely to preponderate against any change which might be brought about by variation of diameter. These remarks, however, were addressed either to single or multiple threads which are in the neighbourhood of 10 denier and upwards.

THE PASSIVE STATE OF IRON.

By JAMES MacLEOD-BROWN.

It is frequently asserted that, if part of an iron nail or wire is rendered passive, the remainder of the nail or wire also assumes this state. That this is not the case is shown by the following experiment.

An iron nail, three inches long, was immersed to a depth of one inch in strong nitric acid. The nail was allowed to drain, and the other end was now immersed to a depth of one inch in dilute nitric acid. It was found that this end of the nail was in the active, or ordinary, state, while the end which had been immersed in the strong nitric acid was found, on testing, to be still passive.

If, however, we render passive part of a nail, by immersing it partly in strong nitric acid, and then lower the nail, passive end first, into dilute nitric acid until it is wholly immersed, it will be found that, after a brisk evolution of gas, which ceases after a second or two, from the part of the nail not rendered passive in the strong nitric acid, that the whole of the nail is in the passive state.

This experiment was repeated with a piece of iron wire shaped like a V. Part of one limb of the V was made passive by immersing it for about half its length in strong nitric acid. The wire was allowed to drain. The part of the limb rendered passive was was now immersed in dilute nitric acid. The other limb of the V was now brought into the dilute nitric acid until about half its length was immersed. After a brisk evolution of gas, which stopped in from two to four seconds, the part of the limb immersed in the dilute acid assumed the passive condition. The apex of the V was now dipped into dilute nitric acid and was found to be active, the parts which had been rendered passive still remaining so.

The same things were observed when a passive iron nail was connected by means of a platinum, or copper, wire to a nail of ordinary iron.

Two iron nails were pushed through a cork which fitted into a test-tube containing dilute nitric acid. One of the nails was rendered passive by strong nitric acid, washed, and allowed to drain. Each of the nails was connected to a terminal of a mirror galvanometer. The nails were now placed into the test tube containing the dilute nitric acid. A deflection of the galvanometer occurred, which decreased until it was zero, when the evolution of gas from the ordinary iron ceased. The direction of the deflection showed that the passive iron was the positive pole and that the ordinary iron was the negative pole.

It was found that, in addition to passive iron, carbon, platinum, and gold, which acted as positive poles, had the power of producing the passive state as described in the previous paragraph. When, however, poles of passive iron obtained by dilute nitric acid, and aluminium or zinc were used, it was found that passivity was destroyed. The aluminium and zinc in this case were the negative poles.

From these experiments it is evident that the passivity produced in the dilute nitric acid is simply due to anodic polarisation. The condition produced when iron is immersed in strong nitric acid may be due to some definite arrangement of the particles at the surface of the iron, as in magnetism. This would explain why passivity vanishes in a magnetic field, inasmuch as the arrangement of the particles would be disturbed. This view is quite probable, because a piece of magnetised iron, where a definite arrangement of the particles at the surface occurs, dissolves more slowly, especially at the poles, than does a piece of ordinary iron.

THE TENDENCY OF ATOMIC WEIGHTS TO APPROXIMATE TO INTEGRAL AND SEMI-INTEGRAL VALUES.*

By ERNEST FEILMANN.

The fact that the atomic weights of the elements so often approximate to integral values, when measured in terms of the usual units, must strike any observer, and has, indeed, given rise to many speculations on the nature of the elements themselves.

The present communication deals with the relations between the deviations of the atomic weights from integral values on the one hand, and the number of elements exhibiting such deviations on the other.

The atomic weights of the International Table for 1913 were rounded off to the nearest tenth of a unit, and then sorted into ten groups according to the magnitude of the decimal portion of the figures so obtained. Where the figure in the table was exactly midway between two values, that is, where the second decimal place had the value 5, the corresponding element was considered to be shared by the two adjacent groups, each of which was credited with half a unit.

The groups were :—

- 0·0 As, Bi, B, C, Cr, Co, Eu, F, He, H, La, Lu, Mo, N, O, P, Na, Sn, Tl, V, Yb, Yt, W—23 elements.
- 0·1 Al, Ca, Gl. Ir, Pb, K, Sc, S, Ti – 9 elements.
- 0·2 Sb, Au, Ne, Pt, Se, Tb, Xe, and Ce (half) 7·5 elements.
- 0·3 Gd, Mg, Nd, Si, and Ce (halt)—4·5 elements.
- 0·4 Ba, Cd, Nt, Ra, Sa, Th, Zn, and Rb (half)—7·5 elements.
- 0·5 Cl, Cb, Dy, Ge, Ho, Ta, Te, Tn, U, and Rb (half-9·5 elements.
- 0·6 Cu, Hg, Pr, Sr, Zr—5 elements.
- 0·7 Er, Ni, Pd, Ru—4 elements.
- 0·8 Cs, In, Fe—3 elements.
- 0·9 A, Br, Ga, I, Kr, Li, Mn, Os, Rh, Ag—10 elements.

Thus we have the following table :—

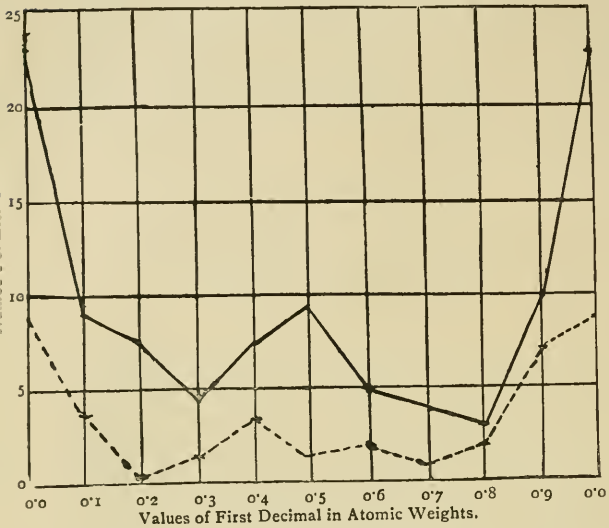
Value of decimal	0·0	0·1	0·2	0·3	0·4	0·5	0·6	0·7	0·8	0·9
Number of elements	23	9	7·5	4·5	7·5	9·5	5	4	3	10

From this table the upper curve (continuous line) in the figure is plotted. The symmetry of this curve is remarkable, considering how many gaps still remain in the periodic table of the elements and other irregularities, such as errors in the atomic weight determinations of the less known elements. The other obvious characters of the curve are, first, the very marked rise as integral values are approached, and, secondly, the smaller maximum in the neighbourhood of 0·5.

Although all the figures given in the atomic weight table might be supposed to be significant, it was thought advisable to plot a further curve, using those atomic weights

* Read before the Chemical Society, November 21, 191 .

only which are given in the table to two or more significant decimals, as it is possible that the large number of atomic weights in the 0·0 column may be really due, to some extent, to the fact that, for the less known elements these



are known only to within about one unit, and that the 0·0 in these cases is really meaningless. We thus obtain the groups:—

0·0 As, C, Co, He, H, N, O, P, Na – 9 elements.
0·1 Ca, Pb, K, S—4 elements.
0·2 Ce (half)—0·5 elements.
0·3 Mg, Ce (half)—1·5 elements.
0·4 Ba, Cd, Zn, Rb (half)—3·5 elements.
0·5 Cl, Rb (half)—1·5 elements.
0·6 Cu, Sr—2 elements.
0·7 Ni—1 element.
0·8 Cs, Fe—2 elements.
0·9 A, Br, I, Li, Mn, Ag, Kr – 7 elements.

From these figures the lower (dotted) curve is obtained.

Considering that the atomic weights of thirty-two elements only are known with sufficient accuracy to be used for this second curve, its general form agrees very well with that of the first curve; there is the same well-marked rise as integral values are approached, and the intermediate maximum is also well-marked, although it coincides with the value 0·4 instead of with 0·5. This fact may, however, well be due to the comparative lack of data.

It appears from the above considerations that there is a marked tendency for atomic weights to approximate to values which are multiples of unity, or, to a less degree, of 0·5, when the present unit, that is one-sixteenth of the atom of oxygen, is used; when the older standard, namely, the atom of hydrogen, is used as unit these relations no longer hold good.

(We are indebted to the Chemical Society for permission to use the woodcut illustrating this article).

Absorption of Ultra-violet Rays by Saturated Fatty Alcohols.—MM. Massol and Faucon.—Methyl and ethyl alcohols are transparent towards the ultra-violet rays for thicknesses up to 10 cm. For propyl alcohol the transparency diminishes slowly with the thickness, while in the case of the higher alcohols the absorption increases with the thickness of the layer of liquid. The transparency diminishes as the number of carbon atoms in the molecule increases. Secondary alcohols are slightly, and tertiary considerably, more transparent than primary alcohols.—*Bull. Soc. Chim.*, xi.-xii., Nos. 20-21.

A SIMPLE EXPERIMENT ILLUSTRATING THE LUMINOSITY OF PHOSPHORUS.

By DOUGLAS F. TWISS.

The following rather striking experiment was devised by me two or three years ago, and as it does not appear to have been previously described in print, it may prove of interest to others.

A vertical glass tube, 2—2½ cm. internal diameter, and about 12 dcm. long, is fitted at the lower end with an indiarubber bung carrying a glass tube, which is bent upwards so as to be parallel to and of approximately the same height as the wider tube. A solution of phosporus in olive oil is introduced into the wider tube so as to reach about 6 inches from the top, and steady suction is applied at the mouth of this tube by means of a water pump. Air enters through the narrow tube and a beautiful series of bell-shaped phosphorescent air bubbles rises through the column of oil.

RARE EARTH REACTIONS IN NON-AQUEOUS SOLVENTS.*

By O. L. BARNEBEY.

1. Introduction.

Very little systematic general analytical work has been done in solvents other than water. Only isolated cases are to be noticed in a review of the subject where application of some non-aqueous solvent has facilitated analytical separations. Among these might be mentioned the ether extraction of iron, the ether extraction of uranium, the separation of barium, strontium, and calcium with alcohol, the ether separation of beryllium and aluminium, the pyridine and the amyl alcohol separation of lithium chloride from sodium chloride. Naumann (*Ber.*, xxxii., 999; xxxvii., 3600, 4328, 4609; xlii., 3789) has studied several reactions, notably the action of hydrogen sulphide and ammonia with most of the common members of the second and third analytical groups in ethyl acetate, methyl acetate, pyridine, and acetone, obtaining very interesting results. The solubility tables of Naumann have been found serviceable, but in error in a number of cases. A new enlarged solubility list will be published in future papers dealing with the analytical chemistry of non-aqueous solvents. This paper is concerned with the domain of the rare earths, dealing essentially with the general reactions of neodymium, lanthanum, cerium, and the yttrium group with various acids and bases,

The usual solvent employed is acetone, although occasionally another solvent is utilised to obtain specific zolubilities not obtainable in this medium. The acetone was carefully dehydrated over calcium chloride for several months, and distilled when needed, only the product with constant boiling-point being employed. The conditions for each reaction have been kept as nearly anhydrous as possible, although small quantities of water are unavoidably introduced in some instances. In such cases the general effect of added water has been carefully considered.

Among the first reactions studied were those with the salts of the halogen acids, and of nitric and sulphuric acids, inasmuch as their corresponding salts are, as a rule, soluble in water.

The iodides of neodymium, yttrium, lanthanum, and cerium are readily soluble in acetone, the bromides moderately soluble, and the chlorides quite insoluble. The nitrates of the earths are soluble, but the sulphates are insoluble in this medium. Hence solutions of the iodides, nitrates, and to a more limited extent the bromides, furnish good solutes for a study of the comparative reactions of the earths in acetone.

* *Journal of the American Chemical Society*, xxxiv., No. 9.

The iodide solutions were prepared by solution of the hydroxides in strong hydriodic acid, evaporation, extraction of the free iodine with carbon disulphide, and solution of the resulting iodides in acetone. The bromide solutions were prepared in the same way, omitting, however, the carbon disulphide treatment. The nitrates were dissolved directly in acetone.

In certain cases reactions do not take place with the nitrates or bromides, but do with the iodides; or do not with the nitrates, but do with the bromides; hence some of the general reactions have frequently been tried with more than one salt dissolved in acetone.

2. General Reactions.

A. *Reactions with Common Acids and Study of the Halides.*

Hydrochloric acid yields insoluble earth chlorides. The acid may be added either by passing the dry gas into the earth solution or by employing a solution prepared by diluting concentrated aqueous hydrochloric acid with a considerable volume of acetone. Upon addition of hydrochloric acid white precipitates of the earth chlorides appear immediately in the form of an emulsion from which crystallisation proceeds slowly and incompletely. The precipitates are soluble in large excess of the reagent. This solvent action is best shown by continuing the passage of gas for some time when complete solution is effected. Dilution with acetone re-precipitates the chlorides.

Yttrium group chlorides are not precipitated by such salts as cupric, stannous, and ferric chlorides in acetone. However, acetone solutions of a number of common chlorides dissolve the solid yttrium group chlorides, which in the absence of chlorides of this character are practically insoluble. Zinc, bismuth, ferric, cupric, antimonous, stannous, cobaltous, and mercuric chloride solutions in acetone dissolve the earth chlorides quite readily. Cadmium, arsenious, and uranyl chlorides act slowly but appreciably. Upon evaporation the copper, cadmium, and cobalt clorides give crystalline products.

Mercuric chloride in acetone added to an acetone solution of yttrium group iodides gives no precipitate immediately, but in a short time a white precipitate of the chloride forms which becomes heavier as more mercuric chloride is added. With excess of mercuric chloride the precipitate re-dissolves to a clear solution. Addition of yttrium iodide solution again causes a precipitate to form, but, on the other hand, an excess of the iodide also gives a clear solution. If the solution is concentrated mercuric iodide precipitates, but this can be avoided by dilution with acetone, in which it is soluble. To ascertain the molecular proportions existing between $HgCl_2$ and YI_3 standard solutions of the two were prepared in acetone. By numerous titrations the following ratios were indicated to exist, although the results are only approximate inasmuch as the end-points were rather obscure: $2YI_3.HgCl_2$, $2YI_3.3HgCl_2$, $YI_3.2HgCl_2$.

The formation of double chlorides indicated above was tried on mixed rare earth chlorides of both the cerium and yttrium groups. Cupric, bismuth, stannous, and ferric chloride solutions in acetone were found to dissolve large quantities of the solid chlorides, although only a very slight amount was soluble in acetone alone. This strengthens the view that double chlorides are formed in solution. On account of the ready solubility of the chlorides in the corresponding solvent it has not been possible to effect a fractionation of the earth by this means.

Crystallisation of double bromides was attempted by evaporating solutions of calcium, cadmium, sodium, and bismuth bromides with the rare earth bromides in acetone solution. The products were of syrupy consistency, and not crystalline. Attempts to crystallise double iodides gave similar results.

Silver nitrate in acetone gives a complete precipitation of the halogens from acetone halide solutions, although the first few drops of reagent cause no precipitate to form. Volhard's method for the estimation of silver or determination of chloride can be carried out in acetone by adding in the above reaction an excess of standard silver nitrate solution in acetone and titrating the excess of silver present with a standard acetone solution of ammonium sulphocyanate, using a ferric salt as indicator. Ferric nitrate crystallised from fuming nitric acid, then dissolved in acetone, can be employed. Thus prepared the ferric solution is only moderately permanent, the iron gradually precipitating. One can prepare a dilute solution of ferric chloride or sulphocyanate and use measured portions for the indicator. Naturally under these conditions a "blank" must be subtracted for the volume of silver nitrate necessary to react with the measured volume of indicator.

Hydrobromic acid precipitates the bromides from concentrated iodide, but not from the nitrate earth solutions. When sodium iodide in acetone is added to a rare earth bromide acetone solution sodium bromide precipitates, the earth iodide remaining in solution.

Hydrofluoric, *sulphuric*, *oxalic*, *citric*, and *mucic acids* precipitate the earths completely as the corresponding salts when acetone solutions of the acids are added to yttrium, neodymium, cerium, or lanthanum nitrates dissolved in acetone.

Tartaric and *phosphoric acids* precipitate the earths almost completely. The phosphates are soluble in large excess of acid. *Malic acid* gives almost complete precipitation upon standing.

Formic, *lactic*, *maleic*, and *succinic acids* give incomplete precipitation of the four earths studied. Lactic acid precipitates the earths completely from the iodide solutions.

Hydrosulphuric, *propionic*, *benzoic*, *salicylic*, *hippuric*, *cinnamic*, or *stearic* acids do not precipitate the corresponding salts of yttrium, neodymium, lanthanum, and cerium. However, the cinnamates, benzoates, hippurates, and stearates are but very slightly soluble in acetone. Stearic acid gives partial precipitation of the earths from the iodide solutions.

Of the above list of reactions those of formic and lactic acids (see tartaric acid fractionation later) merit especial description, inasmuch as they show evidences of being good reagents for separation purposes.

Formic acid diluted with acetone and added to a cerium solution gives a small amount of a white precipitate instantly. On standing this precipitate gradually becomes heavier. Lanthanum precipitates in a like manner. Neodymium yields no precipitate at first with a moderate amount of formic acid, but upon standing a pink precipitate appears. A large excess of formic acid throws down a precipitate at once. No precipitate is obtained using any concentration of acid with the nitrates of the yttrium group in acetone even after allowing to stand for forty-eight hours. The precipitates of cerium, lanthanum, and neodymium are slowly soluble in water. Undoubtedly formic acid could be used as a rapid means of fractionation of the mixed earths.

Lactic acid yields white gelatinous lactates with the nitrates of the yttrium earths. The precipitation is almost complete. The lactates are very soluble in water, and very soluble in dilute ammonia. Stronger ammonia (sp. gr. 0·9) dissolves the lactates, forming two immiscible layers both containing yttrium. Warming re precipitates the earths from the ammoniacal solutions. When lactic acid in acetone is added to a moderately strong solution of cerium nitrate no precipitate appears. Dilution and prolonged standing cause the lactates to settle out. The solubility of the cerium precipitate in water and its deportment with ammonia resemble yttrium. Neodymium precipitates like cerium. Lanthanum is more difficult to throw down with lactic acid, the precipitate forming much more slowly than with cerium or neodymium. The yttrium group precipitates so readily and the others so slowly that without doubt lactic acid can be applied as a rapid fractionation agent for the concentration of this group away from the others.

B. *Reactions with Bases.*

The reaction of a number of organic bases were tried in acetone with the earth nitrates, but they gave no precipitates or general appearance of reaction. Among these were aniline, ethylaniline, acetamide, naphthylamine, diphenylamine, phthalamide, pyridine, quinoline, and urea. Benzylamine gives partial precipitation. Phenylhydrazine added to a concentrated nitrate solution of the earths gives two immiscible layers, the lower layer containing practically all of the earths. The lower layer is slightly pink and is miscible with acetone, hence is not obtained in dilute solutions.

Ammonia Reactions.

When anhydrous NH_3 is passed into an acetone solution of yttrium nitrate, lanthanum nitrate, cerium nitrate, or neodymium nitrate, a heavy white precipitate forms which contains varying amounts of earths, nitric acid, ammonia, and acetone, the first and last named being the highest in percentage composition. These precipitates are difficult to handle, inasmuch as in many cases when desiccation is utilised to free the precipitates from the acetone held in loose combination, decomposition occurs, yielding a dark coloured mass which contains considerably more nitrogen than corresponds to the nitric acid and ammonia content.

The nitrates are not well adapted for the study of this reaction, due to the difficulty of keeping the conditions sufficiently anhydrous. Naturally if water is present in appreciable amounts the hydroxides are formed in part at least. Decompositton due to oxidation is another factor with the nitrates. Some of the compounds obtained were semi-explosive when heated, hence the oxide value could not be obtained by direct ignition. This reaction is being further investigated.

Reactions with the Alkaloids.

Acetone is a good solvent for the alkaloids. When a number of the alkaloids are dissolved in acetone and the acetone solution added to an acetone earth solution. compounds are formed which contain the earth nitrate and the alkaloids, hence they appear to be a new type of alkaloidal compounds.

The quinine compounds of cerium, lanthanum, neodymium, and yttrium are precipitated by the addition of an excess of acetone solution of quinine to the acetone earth solution as white amorphous bodies (the nitrates were employed). The precipitates in the case of yttrium, lanthanum, and neodymium are soluble in the earth nitrates. The cerium compound is precipitated with the first drop of alkaloidal solution, hence is not soluble in excess of earth nitrate. All are soluble in water.

Solutions of lanthanum, cerium, neodymium, and yttrium earth nitrates in acetone were treated separately with acetone solutions of quinine, and the precipitates handled like those with brucine. The acetone is very difficult to remove from the quinine. The compounds $4LaONO_3.C_{20}H_{24}N_2O_2$, $4NdONO_3.C_{20}H_{24}N_2O_2$, $4YtONO_3.C_{20}H_{24}N_2O_2$, and $4CeONO_3.C_{20}H_{24}N_2O_2$ were indicated to exist.

Cinchonidine is sparingly soluble in acetone, hence ethyl alcohol was used as the solvent. An excess of reagent precipitates yttrium, lanthanum, and neodymium slowly. Warming hastens reaction and precipitates cerium immediately. The precipitates obtained with the first three are soluble in excess of earth nitrates, but not so with cerium. All are white compounds, soluble in water.

Cocaine dissolved in acetone yields with the earth solutions white precipitates soluble in water.

Sanguinarine is readily soluble in acetone and yields yellow compounds, forming readily with lanthanum, more slowly with cerium and neodymium, and still more slowly with yttrium. The compounds are soluble in water. The precipitates have a tendency to turn red on standing.

Chelerythrine is readily soluble in acetone and gives yellow precipitates with the earths, with lanthanum quickly, with cerium not so rapidly, with neodymium more slowly and with yttrium still more slowly. The precipitates are soluble in water.

Piperidine is readily soluble in acetone. It gives white precipitates with the earths, which are almost completely insoluble in acetone but are soluble in water.

Hyoscyamine is soluble in acetone. With the earths in excess no precipitate is formed, but with alkaloid in excess white precipitates are obtained. All are soluble in water.

Brucine is readily soluble in acetone. With lanthanum, cerium, and neodymium precipitation ensues immediately with the first drop of alkaloid added and gradually becomes heavier, although complete precipitation does not occur for several days with an excess of alkaloid. Yttrium requires an excess of alkaloid to start precipitation. The products are all white, except that of neodymium, which has a pink tinge. All are soluble in water.

Weak acetone solutions of the nitrates of lanthanum, cerium, neodymium, and the yttrium group were treated with an excess of brucine dissolved in acetone. The precipitates were filtered and washed with acetone by suction, then dried *in vacuo* over potassium hydroxide for several days. The precipitates retained a large amount of acetone which could be satisfactorily removed only by prolonged desiccation under diminished pressure.

Upon analysis the following ratios were found to obtain: $La(NO_3)_3.C_{23}H_{26}N_2O_4$. $2Nd(NO_3)_3.C_{23}H_{26}N_2O_4$, $Yt(NO_3)_3.C_{23}H_{26}N_2O_4$, and $Ce(NO_3)_3.C_{23}H_{26}N_2O_4$. The alkaloid may be functioned as indicated or as basic earth alkaloidal nitrates.

Morphine in acetone gives a white precipitate with the earths, requiring an excess of reagent in case of yttrium, lanthanum, and neodymium, while with cerium the precipitate forms immediately with the first drop of alkaloid solution. The first three compounds are soluble in excess of earth nitrate. All are soluble in water.

Coniine is miscible with acetone in all proportions. Coniine gives a white precipitate with yttrium nitrate, requiring a larger excess of alkaloid than with the other three earths studied. When added to the earth solution in quantity just sufficient to give a permanent precipitate, the precipitate is soluble in water. When added in larger amounts so that the alkaloid is in excess the precipitate is not soluble in water. Neither precipitate is soluble in alcohol. This deportment indicates the formation of at least two compounds.

With lanthanum the reaction is similar except that the precipitate forms with less excess of alkaloid.

With cerium the reaction is also similar to that of lanthanum, but does not show the water-soluble compound to such a marked degree.

With neodymium the reaction is analogous to that of lanthanum.

Strychnine is almost insoluble in acetone, hence a solution in ethyl alcohol was employed. With all four of the earths white precipitates are slowly formed. They are all soluble in water.

Leucine dissolved in warm ethyl alcohol (in which it is only slightly soluble) yields white precipitates soluble in water.

Cinchonine, *narcotine*, and *piperine* give no precipitates with the four earths studied.

(To be continued)

Rotatory Power of Camphor Dissolved in Carbon Tetrachloride.—A. Faucon. — The rotatory power of camphor dissolved in carbon tetrachloride is independent of the time which has elapsed between solution and the observation. It increases with the concentration and also with the temperature. The variation of the rotatory power under the influence of the temperature depends upon the concentration; thus an increase of 1° increases the angular deviation by a larger amount in the case of concentrated solutions than in that of dilute solutions, and the augmentation is greater at about 12° than at 40°.—*Bull. Soc. Chim. de France*, xi.-xii., Nos. 20-21.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, December 5th, 1912.

Dr. M. O. Forster, F.R.S., Vice-President, in the Chair.

Captain G. I. Davys was formally admitted a Fellow of the Society.

The Chairman announced that the Council had decided :—

1. That in order to obtain a more equal division of abstracts, those of Physiological Chemistry and the Chemistry of Vegetable Physiology and Agriculture shall, in future, be included in Part I. of the Abstracts, instead of in Part II.

2. That persons requiring expanded Abstracts or translations of papers published in other Journals should apply to the Editor. Ten shillings per printed page (about 500 words) will be charged, and payment should be made to the Editor at the time the request for a translation or fuller abstract is forwarded to him.

Certificates were read for the first time in favour of Messrs. Theodore William Gull Acland, B.A., 19, Bryanston Square, W.; Albert Brier, M.Sc., 19, Alexander Road, Ulverston; Charles George Cutbush, 59, Byne Road, Sydenham, S.E.; Thomas Lenton Elliott, Lincoln House, Heckmondwike, Yorks; Robert Gilmour, B.Sc., Ph.D., Scores Villa West, St. Andrews; James Arthur Hewitt, B.Sc., 3, South Bridge Street, St. Andrews; William Joseph Holt, 31, Spruce Hills Road, Walthamstow, N.E.; Paul Murphy, Burnside, Sidcup, Kent; Jonathan Harold Naylor, M.Sc., 73, Castle Street, Bolton; Harold Victor Taylor, Royal College of Science, S. Kensington, S.W.; Percy James Thompson, The Avenue, Clytha Square, Newport, Mon.; Thomas Willoughby Turnill, Stibbington, Wansford, Northamptonshire; Edward Webb, B.Sc., Berwyn, Totteridge, Whetstone.

A Ballot for the election of Fellows was held, and the following were subsequently declared duly elected :—Edwin John Amies, B.Sc.; William Llewelyn Baily; James Henry Young Baker; Douglas Anderson Bowak; Edmund Arthur Buckle; Richard Westman Challinor; Frank Andrew Coombs; Walter Henry Dixon; H. H. Dodds, M.Sc.; James Crawford Douglas; James Harry Dyson; Ridsdale Ellis, B.Sc.; George Davidson Elsdon, B.Sc.; Sydney Charles Gadd; Harold Heath Gray, B.Sc.; Frederick Lyle Grützmacher; Arthur James Hale, B.Sc.; Archie Haydon; Edward Hope, M.Sc.; Ardesir Naservanji Peston Jamas, M.A., B.Sc.; Edgar Jobling, B.Sc.; Shigeru Komatsu; Frederick Russell Lankshear, B.A., M.Sc.; Stanley Isaac Levy, B.A., B.Sc.; Ernest Lawson Lomax, M.Sc.; Francis Maxwell; George Francis Morrell, Ph.D., B.Sc.; Ernest Moore Mumford, B.Sc.; Tanjore S. Natrajan; Leslie Frank Newman, B.A.; William Moore Nichols; Maximilian Nierenstein, Ph.D.; Carl Alfred Nowak, B.Sc.; Lionel Orange, B.Sc.; Ramni Paniker, M.A., M.Sc.; John William Patterson; Charles Etty Potter, B.Sc.; Jitendra Nath Rakshit; Martin Remers, L.R.C.P., L.R.C.S.; Herbert Carr Roper; Albert Sasson; Harold Archibald Scarborough, B.Sc.; Walter Scott; Kunjo Behary Seal; Cyril Edgar Sladden, B.A.; Alfred Thomas Smith, B.Sc.; William Charles Smith; Victor Steele; Alfred Ernest Stephen; William Compton Till, M.Sc.; Hui Chun Tsao, B.Sc.; Paul Jenner Ure.

Of the following papers those marked * were read :—

*308. "*Chemical Reactivity and Absorption Spectra.* Part II. *The Variation in Absorption produced by a Solvent.*" By Edward Charles Cyril Baly and Francis Owen Rice.

In two previous papers (*Trans.*, 1912, ci., 1469, 1475) it was pointed out that every chemical molecule must be the centre of a condensed field of force. Each individual atom in any given molecule possesses a certain amount of free affinity, which must be accompanied by the existence of lines of force in its immediate neighbourhood. Inasmuch as there exist two types of this affinity, acid and basic, it follows that the independent existence of these lines of force in a molecule must be a metastable condition, and that the various force lines must condense together with the escape of free energy. The chemical reactivity of the resulting condensed system will be very much reduced, and in some cases may fall to zero. It has been shown how these systems can be unlocked by the action of light, and how the reactivity thereby may be increased. In many cases the closed system can partly be opened by the influence of a solvent, and under the influence of light they may still further be opened. A quantitative measure of the amount of light absorbed by substances at various concentrations in suitable solvents has been carried out.

As a result of this theory it would be expected, in the case when a substance is opened up by a solvent, that the amount of light absorbed should increase with the dilution until a maximum is reached. Further dilution should then cause a decrease in the amount of light absorbed, and finally the solution should become diactinic. This result has experimentally been found.

*309. "*Studies in the Camphane Series.* Part XXXIII. *Orientation of Tiemann's* iso*Aminocamphor.*" By Martin Onslow Forster and Hubert Arthur Harry Howard.

Tiemann's *iso*aminocamphor, produced by the action of hydriodic acid on camphoroxime, was found to have the amino-group in the position occupied by the substituent in β-chlorocamphor, β-bromocamphor, and Reychler's camphorsulphonic acid. It is therefore re-named β-aminocamphor, and by hydrolysing the hydroxycamphor *semicarbazone*, $C_{11}H_{19}O_2N_3$, which arises by exchange of the amino-group for hydroxyl when semicarbazide acetate acts on β-aminocamphor, *β-hydroxycamphor*, $C_{10}H_{16}O_2$, has been prepared; the substance is short-lived, rapidly changing into the isomeric dihydrocampholenolactone.

310. "*A Study of some Organic Derivatives of Tin as regards their Relation to the Corresponding Silicon Compounds.*" By Thomas Alfred Smith and Frederic Stanley Kipping.

As the results of a comparison of optically active derivatives of tin with the corresponding silicon compounds might lead to important conclusions, attempts have been made to synthesise *dl*-dibenzylethylpropylstannanesulphonic acid, $SnEtPr(CH_2{\cdot}C_6H_5){\cdot}CH_2{\cdot}C_6H_4{\cdot}SO_3H$, by methods analogous to those employed in the preparation of dibenzylethylpropylsilicanesulphonic acid (Challenger and Kipping, *Trans.*, 1910, xcvii., 142, 755). These experiments were successful only up to a certain point, for although *dibenzylethylpropylstannane* was, in fact, obtained, the *dl*-monosulphonic derivative of this compound could not be prepared.

The following benzyl and benzylalkyl derivatives of stannic chloride were described : *Dibenzylstannic chloride, bromide, iodide,* and *acetate*; *tetrabenzylstannane, tribenzylethylstannane, dibenzyldiethylstannane,* and *dibenzylethylpropylstannane. Ethylpropylstannic chloride* was also obtained.

311. "*Contributions to the Chemistry of the Terpenes.* Part XV. *Synthesis of a Menthadiene from Carvacrol.*" By George Gerald Henderson and Schachno Peisach Schotz.

Carvomenthol, $C_{10}H_{19}{\cdot}OH$, prepared by hydrogenating carvacrol according to the method of Sabatier and Senderens, yields Δ^1-menthene, $C_{10}H_{18}$, when heated with anhydrous oxalic acid. The hydrocarbon forms an oily dibromide, $C_{10}H_{18}Br_2$, which, when heated with alcoholic potassium hydroxide or with anhydrous sodium acetate and acetic acid, is converted into a *menthadiene*, $C_{10}H_{16}$, a

colourless liquid with a pleasant odour, which boils at 172—174°.

It was expected that the product of these reactions would be either α- or β-phellandrene, but this was not the case; at least, it could not be converted into a nitrite. On the other hand, the menthadiene obtained in this way from carvacrol has considerable resemblance to the corresponding hydrocarbon formerly obtained from thymol by a similar process, although it has not been proved that they are identical.

312. "*The Action of Halogens on Silver Salts.*" By Hugh Stott Taylor.

Iodine reacts with silver salts in a manner analogous to that observed in reactions with chlorine and bromine, to yield insoluble silver iodide, hypoiodous acid, and another acid. The reaction occurring may be represented by the equation: $AgX + I_2 + H_2O = AgI + HIO + HX$.

Owing to the instability of hypoiodous acid, a second reaction occurs, accelerated by rise of temperature, increase in concentration, or presence of soluble silver salts, in which the hypoiodous acid is converted into iodide and iodate. This secondary reaction may be generally represented thus: $3HIO + 3AgX = 2AgI + AgIO_3 + 3HX$.

The progress of this second reaction has been followed in various concentrations of the reacting solutions.

The simple equation of Birnbaum (*Annalen*, 1869, clii., 111) and of Normand and Cumming (*Trans.*, 1912, ci., 1852), $3I_2 + 3H_2O + 6AgX = 5AgI + {}_3 + AgIO_3 + 6HX$, represents the sum of the two preceding equations.

313. "*The Formation of Tetrahydro-oxazoles from α-Hydroxy-β-anilino-αβ-diphenylethane and its Homologues.*" By Horace Leslie Crowther and Hamilton McCombie.

Tetrahydro-oxazoles cannot be prepared from the dihydro-oxazoles described by McCombie and Parkes (*Trans.*, 1912, ci., 1991) by simple reduction. If, however, α-keto-β-anilino-αβ-diphenylethane is reduced to the corresponding hydroxy-compound (I) by means of sodium amalgam in alcohol, this compound then undergoes condensation with carbonyl chloride to yield 3 : 4 : 5-*triphenyl*-2 : 3 : 4 : 5-*tetrahydro* 2-*oxazolone* (II.):—

I. II.

Similar compounds have been prepared from the corresponding *m*- and *p*-toluidines and β-naphthylamine analogues of (I.).

The tetrahydro-oxazoles obtained are very stable substances, which resist the action of reducing agents and phosphorus trichloride, and do not form salts with hydrochloric acid or with picric acid.

Attempts were also made to condense α-hydroxy-β-anilino-αβ-diphenylethane and its homologues with thionyl chloride and sulphuryl chloride, but these were unsuccessful.

314. "*The Precipitation of Lead Thiosulphate and its Behaviour on Boiling with Water.*" By William Hughes Perkins and Albert Theodore King.

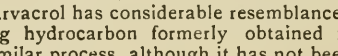
The addition of sodium thiosulphate to a solution of lead acetate produces a precipitate the composition of which varies with the dilution of the solutions, and with the proportions in which they are mixed. From concentrated solutions, especially those containing excess of the lead salt, the precipitate consists of the double salt $Pb(C_2H_3O_2)_2,2PbS_2O_3$, whilst from dilute solutions or with excess of thiosulphate it has a composition corresponding with PbS_2O_3. It is therefore advisable when pure lead thiosulphate is required to obtain it from lead nitrate. The well-known blackening of this salt on warming takes place most readily in the presence of excess of sodium thiosulphate according to the equation—

$$PbS_2O_3 + 3Na_2S_2O_3 = PbS + {}_4S + 3Na_2SO_4.$$

Without the sodium salt the reaction is slower and more complex, but it still proceeds mainly according to the equation $4PbS_2O_3 = PbS + 4S + 3PbSO_4$. The authors' results are in conflict with those of Fogh (*Ann. Chim. Phys.*, 1890 [6], xxi., 56), who prepared his thiosulphate from moderately concentrated lead acetate solution, and represented its decomposition on boiling by the equation $2PbS_2O_3 = PbS + PbS_3O_6$.

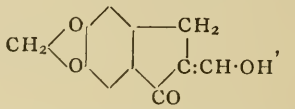
315. "*Studies on Cyclic Ketones.*" (Part II.) By Siegfried Ruhemann and Stanley Isaac Levy.

The work on cyclic ketones (Ruhemann, *Trans.*, 1912, ci., 1729) has been continued on the same lines as before; in particular, the authors have examined the hydroxymethylene derivatives of various cyclic ketones. They find that 2-*hydroxymethylene*-1-*hydrindone*,—

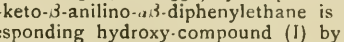


a colourless solid soluble in alcohol, undergoes on warming a remarkable transformation, involving the elimination of one molecule of formic acid from two molecules of the substance; the condensation product,—

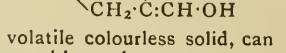
is a deep red solid, insoluble in alcohol and decomposing at 232°. The corresponding methylenedioxy-derivative,—



undergoes the same change at a somewhat higher temperature; but the hydroxymethylene derivatives of 1 : 3-dimethyl-Δ^3-*cyclo*hexen-5-one,—



which is a yellow oil, and of 1-methyl*cyclo*pentan-3-one,—



which is a very volatile colourless solid, can both be distilled in a vacuum without change.

In other respects the hydroxymethylene derivatives of the hydrindone series resemble those already examined by Claisen and his pupils; thus they yield green copper salts, and anilides, and react with semicarbazide, and with phenylhydrazine, in the latter case forming pyrazole derivatives.

316. "*Some Hydrogen Ferrocyanides.*" By Herbert Ernest Williams.

By treating solutions of the ferrocyanides of the alkali or alkaline earth metals with hydrochloric acid, ferrocyanic acid is liberated.

The ferrocyanides of the heavy metals, however, behave differently; thus, when cupric ferrocyanide is boiled with concentrated hydrochloric acid, half of the copper is replaced by hydrogen, and there is obtained a yellow insoluble *cupric hydrogen ferrocyanide*, $CuH_2Fe(CN)_6,4H_2O$.

In a similar manner, but with slight variation of conditions, such as lower temperature or diluted acid, double hydrogen salts of nickel, cobalt, manganese, zinc, and cadmium can be obtained.

By these means the following compounds have been prepared and examined: *Cobalt hydrogen ferrocyanide*, $CoH_2Fe(CN)_6,4H_2O$; *manganese hydrogen ferrocyanide*, $MnH_2Fe(CN)_6,5H_2O$; and *nickel hydrogen ferrocyanide*, $NiH_2Fe(CN)_6,3H_2O$.

These acid salts are insoluble in water, and decompose alkali carbonates readily with liberation of carbon dioxide, and when digested in solutions of the chlorides of the alkali metals, hydrochloric acid is liberated.

The cupric salt, when digested with solutions of potassium or ammonium chlorides, liberates two equivalents of

hydrochloric acid, and forms the corresponding cupric potassium or cupric ammonium ferrocyanide respectively.

With potassium chloride the reaction is represented by the equation $CuH_2Fe(CN)_6 + 2KCl = CuK_2Fe(CN)_6 + 2HCl$.

With sodium chloride solution in the cold only half the hydrogen of the copper compound is replaced, thus: $CuH_2Fe(CN)_6 + NaCl = CuNaHFe(CN)_6 + HCl$, forming the triple salt, *cupric sodium hydrogen ferrocyanide*, which has a dirty brown colour. When this triple salt is digested in a solution of potassium or ammonium chloride, the remaining hydrogen atom is replaced, forming one equivalent of hydrochloric acid and cupric sodium potassium or cupric sodium ammonium ferrocyanide respectively.

317. "*The Formulæ of Ipuranol and some Related Compounds.*" By Frank Tutin and Hubert William Bentley Clewer.

In a paper published some time ago (*Amer. J. Pharm.*, 1908, lxxx., 264) Power and Rogerson described the isolation from *Ipomœa purpurea* of a substance which was designated ipuranol, and since then the same compound has repeatedly been obtained from a variety of plants. The analysis of the ipuranol, and of its acetyl derivative, appeared to indicate that the substance in question was a dihydric alcohol possessing the formula $C_{23}H_{38}O_2(OH)_2$. It has since been observed, however, that the analytical results agree equally well for a higher formula, $C_{29}H_{47}O_2(OH)_3$. The present authors have recently analysed benzoylipuranol, when figures were obtained which were not in harmony with the formula $C_{23}H_{38}O_4(CO{\cdot}C_6H_5)_2$, but were in exact agreement with those theoretically required for the tribenzoyl derivative of a substance possessing the higher formula mentioned above. In the following table the theoretical analytical figures for the two formulæ are compared :—

Required for—	$C_{23}H_{38}O_2(OH)_2$.	$C_{29}H_{47}O_2(OH)_3$.
Alcohol	C = 72·6, H = 10·5	C = 72·8, H = 10·5
Acetyl derivative .	C = 69·8, H = 9·5	C = 69·5, H = 9·2
Benzoyl derivative	C = 75·5, H = 8·2	C = 76·0, H = 7·8

A molecular-weight determination of the acetyl derivative was subsequently made, when the value 607 was obtained, compared with 604 required for $C_{29}H_{47}O_5(CO{\cdot}CH_3)_3$ and 464 required for $C_{23}H_{38}O_4(CO{\cdot}CH_3)_2$. It is thus evident that ipuranol is a trihydric alcohol, possessing the formula $C_{29}H_{47}O_2(OH)_3$.

Similarly, it has been ascertained that cluytianol possesses the formula $C_{29}H_{46}O(OH)_4$, and not $C_{23}H_{37}O(OH)_3$, as recently stated (*Proc.*, xxviii., 265).

Power and Moore (*Trans.*, 1910, xcvii., 102) described the isolation from colocynth of a new alcohol, designated as citrullol, which appeared to possess the formula $C_{22}H_{36}O_2(OH)_2$, thus being a lower homologue of ipuranol. A small quantity of this substance being available, it has now been re-investigated, with the result that it has been ascertained that citrullol should be represented by the formula $C_{28}H_{45}O_2(OH)_3$, a conclusion which is quite in harmony with the analytical results obtained by Power and Moore. The citrullol examined was analysed, with the following result :—

0·0923 gave 0·2448 CO_2 and 0·0859 H_2O. C = 72·3 ; H = 10·3.
$C_{28}H_{48}O_5$ requires C = 72·4 ; H = 10·3 per cent.
Power and Moore found C = 72·1 ; H = 10·4 per cent.

A molecular-weight determination of the acetyl derivative yielded the following result :—

0·4019 in 23·96 benzene gave Δt − 0·13°. M.W. = 613.
$C_{34}H_{54}O_8$ requires M.W. = 590. $C_{26}H_{42}O_6$ requires M.W. = 450.

Benzoylcitrullol has not previously been described. It forms colourless needles, melting at 179—180° :—

0·0947 gave 0·2640 CO_2 and 0·0650 H_2O. C = 76·0 ; H = 7·6.
$C_{49}H_{60}O_8$ requires C = 75·8 ; H = 7·6 per cent.
$C_{36}H_{46}O_6$,, C = 75·2 ; H = 8·0 ,,

In view of these results it would appear probable that some, at least, of the other alcohols related to ipuranol which have been isolated may possess higher formulæ than those at present ascribed to them, but material for their re-investigation is not now available.

318. "*Molecular Conductivity and Ionisation of Nitrites.*" By Prafulla Chandra Ray and Nilratan Dhar.

Twenty-three nitrites have been studied from the point of view of their electrical conductivity and hydrolysis in aqueous solution. The nature of the complexes in the salts sodium mercurinitrite, $Na_2Hg(NO_2)_4$, tetramethylammonium mercurinitrite, $NMe_4Hg(NO_2)_3$, and mercurosomercurinitrite, $HgHg_2(NO_2)_5$, has been determined.

The inadequacy of the expression $A_v/A_0 = \mu$ was also discussed.

319. "*The Latent Heats of Chloroform and Benzene and of their Mixtures between 0° and 80°.*" By James Fletcher and Daniel Tyrer.

A method was described for accurately determining latent heats at constant composition of mixtures over a wide range of temperature. The latent heats of pure chloroform and pure benzene and mixture of these liquids of varying compositions have been determined between the ordinary temperature and the boiling points. It is found that for any given mixture the latent heat is a linear function of the temperature, and for a given temperature the latent heat is approximately a linear function of the composition.

320. "*Synthetic Aminoglucosides Derived from d-Glucosamine.*" By James Colquhoun Irvine and Alexander Hynd.

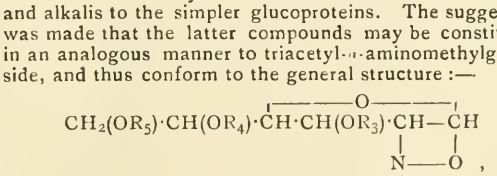
It was shown that bromotriacetylglucosamine is a general reagent for the preparation of α-aminoglucosides, as it enters into reaction with widely different types of hydroxy-compounds, giving, in the first instance, acetylated aminoglucosides, from which the acyl groups may be removed by hydrolysis.

Both the acetylated and unsubstituted aminoglucosides thus obtained may be divided into two classes, which differ in their behaviour towards hydrolytic agents, and in their capacity to form molecular complexes with metallic haloids. Some of the compounds are remarkably stable, and are only hydrolysed to give glucosamine salts when strongly heated with concentrated acid. In such cases they are also unaffected by enzymes, and form additive compounds with silver iodide.

α-Aminoglucosides of this nature are regarded as cyclic nitrogen compounds of the general type described in a previous paper (*Trans.*, 1912, ci., 1128). The examples of this class now described are *α-aminoethylglucoside* and *α-aminoamylglucoside*.

A second type of aminoglucoside is formed when the group combined with the glucosamine residue contains a benzene ring, as then hydrolysis with dilute mineral acids proceeds quite normally, and thus the usual glucosidic formulæ may be applied to the compounds. Representative members of this class are *α-aminobenzylglucoside*, *α-aminohelicin*, *α-aminosalicin*, and *α-aminomorphineglucoside*.

In many respects acetylated aminoglucosides show a remarkable similarity in their behaviour towards both acids and alkalis to the simpler glucoproteins. The suggestion was made that the latter compounds may be constituted in an analogous manner to triacetyl-α-aminomethylglucoside, and thus conform to the general structure :—



where G stands for the "glucosidic" group, and R_1, R_2, &c., for amino-acyl residues. Syntheses of complexes of this nature are now being carried out.

NOTICES OF BOOKS.

Outlines of Physical Chemistry. By G. Senter, D.Sc. (Lond.), Ph.D. (Leipzig). Third Edition. London: Methuen and Co., Ltd. 1912.

A very short period of time has elapsed since the first publication of this book, which at once met with the success it thoroughly deserved as an elementary text-book of physical chemistry. In the third edition the most important alterations are firstly the fuller treatment of Colloidal Solutions, which could be adequately discussed in two pages in the first edition, whereas now a whole chapter is devoted to their preparation and properties and to the consideration of the phenomenon of adsorption. Secondly, a useful collection of problems has been added. In these problems references to the text and occasionally hints for solution are given, as well as the answers.

Leather Chemists' Pocket-book. Edited by Prof. H. R. Procter, M Sc., F.I.C., F.C.S., assisted by Edmund Stiasny, Ph.D., and Harold Brumwell. London: E. and F. N. Spon, Ltd. New York: Spon and Chamberlain. 1912.

This book is intended for use as an adjunct to Prof. Procter's "Leather Industries Laboratory Book," and is based upon manuscript sheets which have been for some time in constant use by the students in the Leather Department of the University of Leeds. It follows the order adopted in the larger work, and gives succinct directions for the analysis of water, the recognition and estimation of tannins, oils, and fats, and the analysis of leather, and, although the subject is treated from an elementary point of view, the book will probably be found quite comprehensive enough for the use of the average student, while the practising chemist, who will also find it valuable for its clear directions and hints on the choice of methods and working details, can when necessary refer to the Laboratory Book for fuller information and for the discussion of the theoretical aspects of the analytical work relating to the leather trades.

Transactions of the American Institute of Chemical Engineers. Volume IV. 1911. New York: D. van Nostrand Company. London: E. and F. N. Spon, Ltd. 1912.

This volume contains the full reports of the meetings of the American Institute of Chemical Engineers held during 1911, and the addresses and papers read before the Institute are also reproduced in it. Many of these relate to subjects of international interest, as for example the Presidential Address, by Dr. F. W. Frerichs, on Some Problems in Chemical Engineering Practice. Others deal at great length with the reports of the Committee on Chemical Engineering Education in America, and with the Patent System in the United States.

Second Stage Inorganic Chemistry (Theoretical). By G. H. Bailey, D.Sc.(Lond.), Ph.D.(Heidelberg). Fourth Edition. London: University Tutorial Press. 1912.

In the fourth edition of this book a chapter, which will repay careful study and thorough assimilation, on the theory of qualitative analysis has been added, and some parts of the original text which dealt with organic chemistry have been omitted. The book completely covers the syllabus of the Lower Examination in Inorganic Chemistry of the Board of Education, and also deals with some subjects which are not required in that examination. Thus there is a short, but clear and interesting, chapter on radio-activity, and the outlines of crystallography and of spectrum analysis are also discussed.

Electricity made Plain. By George R. Peers. Manchester and London: John Heywood, Ltd.

The general public with no special scientific knowledge is perhaps more interested in electricity and its applications in everyday life than in any other sciences, and any book which throws light upon its apparent mysteries in non-technical language, if reasonably well written, should be sure of meeting with success. But the author of this book does not appear to be as capable of putting himself in the place of the unitiated reader and explaining from his point of view as the writer of popular scientific books should be. Nor are his statements always above reproach of inaccuracy; for instance, he speaks of those terms known as "Ohm's Law, and they are: — Volt, Ohm, Ampère," and the actual law is never stated, though it is used in calculations. Moreover, the diagrams which are lettered but not explained, would frequently convey absolutely nothing to the reader. The author pays a good deal of attention to financial statistics and details, and treats fairly fully the applications of electricity in medicine.

Metropolitan Borough of Poplar. Annual Report for the Year 1911. By Fredk. Wm. Alexander.

This Annual Report contains interesting information concerning the electrolytic disinfecting fluid which is distributed gratis in the Borough of Poplar. The report gives statistics of its consumption, which is continually increasing, and the adverse criticisms which have been directed against it are commented on. A brief account is given of its manufacture and of the special difficulties which had to be overcome when the manufacturing plant was first installed.

La Teinture du Coton. ("The Dyeing of Cotton"). By E. Serre. Paris: H. Dunod and E. Pinat. 1912.

This book contains a detailed account of the processes employed in the dyeing and printing of cotton. The history and theory of dyeing are first briefly discussed, and then the properties of water, sulphuric acid, caustic soda, sodium sulphate, and various other raw materials used in the industry are described. Methods of preparing some important substances are given, with a certain amount of analysis and quantitative work. In the second part the treatment of the cotton before dyeing is first discussed, and the different dyes—substantive, basic, alizarine dyes, indanthrene dyes, &c.—are then considered in turn with considerable completeness. Full instructions are included for the use of each dye, and specimens of the tints produced are also given.

Das Erdöl. ("Petroleum.") Edited by C. Engler and H. V. Hofer. Volume I., Part I. By C. Engler. Leipzig: S. Hirzel. 1912.

This treatise on petroleum, which is the work of a number of authors in collaboration and is to be complete in five volumes, aims at giving an exhaustive account of the geology, physics, chemistry, and technology of petroleum, surpassing in comprehensiveness and fulness of detail any other treatise in the German language. In the first volume the results of the physical and chemical examination of petroleum and its allied products are given. Original papers and articles are examined critically, and every effort has been made to sift thoroughly all the great mass of detail which has been accumulated and to pass over no results which are well-attested and of undoubted accuracy. In the early part of the book chapters are devoted to certain phenomena and processes which play an important part in the production, purification, or employment of petroleum, such as catalysis, dissociation, polymerisation, &c., but by far the greatest part of the book deals with petroleum itself, its behaviour on heating and towards reagents, its constituents, and its physical properties, and it would be difficult to suggest any amplification or extension which could add to its value.

V. Congrès International de Photographie. ("Fifth International Congress of Photography"). Edited by Ch. Puttemans, L.P. Clerc, and E. Wallon. Brussels: Emile Bruyant. 1912.

The proceedings of the fifth International Congress of Photography, held at Brussels in the summer of 1910, are given in full in this volume. The congress was divided into three sections dealing with subjects of a scientific and technical nature and with the reproduction of documents, &c., by photography, and many questions of interest both to amateur and professional photographers were discussed at the meetings. All memoirs and communications addressed to the congress are also reproduced in full, those which were in foreign languages having been translated into French. These papers include one by Prof. Zeeman on radiation in a magnetic field, and many of them are well illustrated by diagrams and photographs.

Handbuch der Presshefenfabrikation. "Handbook of the Manufacture of Pressed Yeast"). By Dr. Wilhelm Kibe. Braunschweig: Friedr. Vieweg und Sohn. 1912. (M. 24).

The pressed yeast industry is growing very rapidly both in magnitude and in importance, and there appears to be no reason to think that it will not see even greater extension in the near future owing to the increased use of its valuable by-product, raw spirit. This text-book for students and practical men by an author who has a very wide knowledge of the scientific questions involved in the preparation of pressed yeast, in addition to a lengthy experience of its manufacture on a large scale, will fill a gap in literature which has existed for many years, for the last treatise on the subject, Otto Durst's "Handbuch der Presshefenfabrikation" has for some time been decidedly out of date. The manufacture of yeast is treated very fully both from a technological and scientific point of view, and, far-reaching and complicated as the subject is, the author has been very successful in producing a really comprehensive account of it.

OBITUARY.

WILLIAM BETTEL.

The chemical world of Johannesburg, and indeed of South Africa generally, is to-day considerably poorer by the death of Mr. William Bettel. Mr. Bettel's work in this country is well known, and it may be of interest to give a short summary of his technical training and career before his arrival on the Rand. From 1869 to 1872 he was a pupil-assistant in the laboratory of Messrs. B. Samuelson & Co., Newport Iron Smelting Works, Middlesbrough-on-Tees. He attended the summer courses at the Royal College of Science, London, under the late Sir Edward Frankland during the years 1872 to 1873. In 1875, at the early age of twenty-one, he was appointed Public Analyst to the Borough of Middlesbrough, which appointment was confirmed the following year by the Local Government Board. The years 1874 and 1875 saw Mr. Bettel appointed Gas Examiner to the Corporation of Middlesbrough and Water Examiner to several urban and rural sanitary authorities. From 1873 to 1879 he practised all branches of his profession, and gained an invaluable experience. Depression in the iron trade and excessive competition caused him to leave Middlesbrough in 1879, and he went to Worcester, where for two years he was associated with Dr. Horace Sweete, who was then public analyst for eight districts. From 1881 to 1882 he was assistant to Edward Riley, F.I.C., analytical and consulting chemist and metallurgist, London. He returned north in 1882, and was until 1885 metallurgist and chief chemist to the Sheffield Smelting Co., and from 1885 to 1889 he occupied a similar position in a similar works in Birmingham. From 1889 to 1892 he was engaged as works manager, metallurgist, and chemist to the Morfa Copper Works and Williams Copper Syndicate, Ltd., Swansea. In 1892 he came to the Rand, and was first employed as chemist to the Robinson G.M. Co. Mr. Bettel was one of the founders of the Chemical, Metallurgical, and Mining Society of South Africa, and was the first president in 1894-5. The proceedings up to the time of the war contain a large number of contributions from his pen, and many of his methods have become classic. Of late years he had been a frequent contributor to the *South African Mining Journal*, and occasionally to the Chemical News, London. He was a member of the recently-formed South African Association of Analytical Chemists, and until recently acted as an alternate on the Council.—*S. African Mining Journal.*

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clv., No. 22, November 25, 1912.

Chemical Reactions of β-Gold. Crystallised Gold.—M. Hanriot and F. Raoult.—Brown gold is rapidly attacked by nitric acid, and the solution contains the nitrate $(NO_3)_3Au.Aq$. The action of hydrochloric acid on brown gold leads to the formation of auric chloride, $AuCl_3$, mixed with a little aurous chloride, AuCl. In a neutral medium auric chloride hardly attacks brown gold, but in presence of hydrochloric acid solution occurs rapidly. When such a solution is cooled it deposits gold in crystals, partly rhomboid tetrahedra and partly dodecahedra. If the magnetic susceptibility of crystallised gold is examined it is found that it consists exclusively of the β-variety. Gold chloride appears to be a separating reagent for the two varieties of gold, one at least of which can be obtained in a pure state.

Carpiline, a New Alkaloid from Jaborandi.—E. Léger and Ferdinand Roques.—When the basic mixture obtained from *Pilocarpus microphyllus* is converted into nitrate or hydrochloride, a certain number of bases remain in the mother liquors, and if these bases are precipitated a new alkaloid carpiline is concentrated in the first fractions. It crystallises in colourless anhydrous prisms which melt at 184—185°. It is soluble in chloroform, benzene, and boiling water, and slightly soluble in ether. Its formula is $C_{16}H_{18}N_2O_3$. It is a very feeble base, and its salts do not reduce potassium permanganate in the cold; the base is therefore saturated. Like pilocarpine it possesses a lactone function, and from its reactions it appears to contain the groups $C_8H_{11}N_2$, $C_6H_5—CH<$, $-OH$, and $\begin{matrix}—CO\\|\\—O.\end{matrix}$ Its toxic action is very slight, and it does not act on the secretions in the same way as pilocarpine.

Influence of Radio-activity on the Development of Plants.—J. Stoklasa.—From the study of the germination and development of seeds of *Triticum vulgare*, *Hordeum disticum*, &c., the author has found that the effect of radioactive water is to hasten germination and promote the growth of leaves and roots to an extraordinary degree. The radio-active waters of Joachimsthal hinder the development of certain micro-organisms, such as *Bac. mycoides* and *Bac. fluorescens liquefaciens*. The only exception which has been met with is *Azotobactar chroococcum*, which is

capable of assimilating gaseous nitrogen, and on the development of which radio active water has a less powerful effect than on other bacilli.

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Atti della Reale Accademia dei Lincei.
Vol. xxi. (ii.), No. 8, 1912.

Acyl Derivatives of α- and β-Amino-pyridines.—F. Carlo Palazzo and G. Marogna.—It has already been shown by Palazzo and Tamburini that α-amino-pyridine can be converted by the action of aceto-acetic or benzoyl-acetic ether into a product of formula $(C_5H_4N)NH.CO.CH=C.OH.R$, which can be dehydrated by means of sulphuric acid to give the dicyclic compound $(C_5H_4N)(NH.CO.CH=CR)$, derived from 1.8-naphthyridine. β-Amino-pyridine reacts similarly with aceto-acetic or benzoyl-acetic ether, but the yield of naphthyridonic derivative is small because sulphuric acid brings about by-reactions.

Action of Sodium Alcoholates on Carbopyrolic Ethers.—U. Colacicchi and C. Bertoni.—From the study of the action of sodium ethylate on alkyl pyrrols it has been found that the tetra-alkyl and tri-alkyl products having a free α-position can easily be characterised by means of their picrates, while the identification of the tri-alkyl products having a free β-position is difficult, since they do not readily give solid derivatives. By acting on 2.3.5-trimethyl pyrrol with methyl magnesium iodide and benzoyl chloride the authors have obtained the corresponding benzoyl derivative with the COC_6H_5 in the β-position. It is a crystalline substance melting at 172—173°.

Thermic Analysis of Binary Mixtures of Chlorides of Divalent Elements.—Carlo Sandonnini.—Zinc chloride gives with strontium chloride a compound $SrCl_2.ZnCl_2$, which decomposes on fusing. With barium chloride a similar compound, $BaCl_2.ZnCl_2$, is obtained. With mercuric chloride two liquid layers are formed. Zinc chloride and manganous chloride do not give solid solutions.

MISCELLANEOUS.

Royal Institution.—On Tuesday next, January 14th, at 3 o'clock, Prof. Bateson begins a course of six lectures at the Royal Institution on "The Heredity of Sex and Cognate Problems"; on Thursday, January 16th, Mr. Seton Gordon delivers the first of two lectures on "Birds of the Hill Country"; and on Saturday, January 18th, Dr. H. Walford Davies commences a course of three lectures, with musical illustrations, on "Aspects of Harmony"—(1) Chord Progression, (2) Added Dissonance, (3) The New Whole Tone Chord and its Predecessors. The Friday Evening Discourse on January 17th will be delivered by Prof. Sir J. J. Thomson on "Further Applications of the Method of Positive Rays"; on January 24th, by Prof. J. O. Arnold, on "Recent Advances in Scientific Steel Metallury"; and on January 31st, by Mr. George H. Trevelyan, on "The Poetry and Philosophy of George Meredith."

"Tempered Copper" Tools.—According to the *Engineering and Mining Journal*, vol. xciii., No. 20, p. 986, the copper cutting instruments of the Tarascans, found in the Balsas River ruins in Guerrero, are so hard that they would turn the edge of a modern knife, and it has been claimed that these people, along with the Aztecs and Toltecs, possessed the secret of tempering copper. On the other hand, copper knives and axes, found at Atcopotzalco, are so soft that they can be cut with an ordinary pocket knife. Analysis showed that in all three localities the copper implements were of the same composition as the copper ores found therein. The blades from Guerrero, which are hard and apparently tempered, were made from the natural ore carrying nickel and cobalt, thus rendering the smelted alloy steel-like in hardness. Thus, the natural product gave an alloy of great hardness when heated and sharpened, while the other ores of practically pure copper, when smelted, resulted in implements which were soft and inferior in cutting value. The sharp cutting implements were therefore the result of Nature's handiwork, and it is indeed very questionable whether these people possessed the secret of tempering.—*Journal of Industrial and Engineering Chemistry*, iv., No. 7.

Artificial Rubber from Seaweed.—A product, now being marketed under the name "Seagumite," said to be non-inflammable, damp-proof, and unaffected by heat or cold, and to be expected to provide a substitute for rubber and leather, is the subject of a patent recently issued to J. S. Campbell, of London (English Patent 5395, 1911). His invention relates to improvements in the production of a substance having the characteristics of rubber and capable of vulcanisation. It had previously been proposed to treat marine plants, lixiviated by acidulated water, with alkalis such as ammonia; and it is said that the material thus produced has, after impregnation with siccative oil or dissolved indiarubber, been found suitable for use in the whalebone industry. The Campbell process consists in boiling washed and crushed seaweed in steam-jacketed pans with ammonia for about 45 hours, 1 gallon of ammonia (specific gravity, 0·88) being used for 5 cwts. of seaweed; drying in an agitating apparatus, to which heat is applied, and during agitation adding 1 gallon of a mineral or vegetable oil, as rosin oil; adding next a vulcanising substance, such as sulphur, and subsequently mixing the whole mass with 25 per cent by weight of a glutinous or resilient binder, as pontianac gum, jelutong, gutta-percha, or reclaimed rubber waste. The whole is then heated for one hour, and finally dried in a vacuum pan or press. Prior to removing and drying, a preservative, as wood or bark extract, may be added to the amount of 0·85 per cent by weight of the seaweed used. The Campbell process seems to be primarily dependent upon the formation of ammonium alginate. Algin in its soluble forms is recognised as having probable value as an agglutinant, and a substance resembling gutta-percha may be prepared from the alkaline alginates and shellac.—*Journal of Industrial and Engineering Chemistry*, iv., No. 7.

MEETINGS FOR THE WEEK.

Tuesday, 14th.—Royal Institution, 3. "The Heredity of Sex and some Cognate Problems," by Prof W. Bateson, F.R.S.

Wednesday, 15th.—Royal Society of Arts, 8. "The Present Condition and Future Prospects of the British Sea Fisheries," by J. Travis Jenkins, D.Sc., &c.

—— Microscopical, 8. Presidential Address, "*Bedellus immortalis*," by H. G. Plimmer.

Thursday, 16th.—Royal Society of Arts, 4.30. "Agricultural Progress in Western India," by G. F. Keatinge, C.I.E.

—— Royal Institution, 3. "Birds of the Hill Country," by Seton Gordon, F.Z.S.

—— Royal Society. "Effect of Junctions on the Propagation of Electric Waves along Conductors," by Lord Rayleigh. "Influence of Chemical Constitution upon Interfacial Tension and upon the Formation of Composite Surfaces," by W. B. Hardy. "Duration of Luminosity of Electric Discharge in Gases and Vapours," by Hon. R. J. Strutt. "Some Electrical and Chemical Effects of the Explosion of Azoimide," by P. J. Kirkby and J. E. Marsh. "Negative After-images with Pure Spectral Colours," by G. J. Burch. "Factors affecting the Measurement of Absorption Bands," by H. Hartridge. "New Method of Measuring the Torque produced by a Beam of Light in Oblique Refraction through a Glass Plate," by G. Barlow "Positive Ionisation produced by Platinum and by certain Salts when Heated," by F. Horton. "Refraction and Dispersion of the Halogens, Halogen Acids, Ozone, Steam, Oxides of Nitrogen and Ammonia, and on the Causes of the Failure of the Additive Law," by C. and Maude Cuthbertson. "Liquid Measurement by Drops," by R. Donald. "The New Theory of Integration," by W. H. Young.

Friday, 17th.—Royal Institution, 9. "Further Applications of the Method of Positive Rays," by Prof. Sir J. J. Thomson, O.M., F.R.S., &c.

Saturday, 18th.—Royal Institution, 3. "Aspects of Harmony," by H. Walford Davies.

THE CHEMICAL NEWS.

Vol. CVII., No. 2773.

EARLY WORK ON HYDROFLUORIC ACID AND THE ISOLATION OF FLUORINE.

By F. D. CHATTAWAY.

Fluor-spar, or as it is sometimes called phosphoric-spar, has been known from very early times. Its names are derived from its ready fusibility, which makes it useful in smelting operations, and from its singular property of becoming luminous when heated. In 1670, Schwanhardt (or Schwankhardt), in Nuremberg, noted that when fluor-spar was heated with oil of vitriol the vapours given off etched glass. Little further was discovered about the mineral until Scheele* more than a hundred years later took up its study. Scheele recognised the presence of lime, and showed that a peculiar acid was expelled from it by the action of "vitriolic acid." He never obtained the acid in a pure state, and as he generally used glass vessels he was much perplexed by obtaining a deposit of silica in the receiver when he passed the acid fumes into water. He considered that a portion of the fumes when passed into water changed into siliceous earth, while another portion condensed and formed with the water a peculiar acid. This latter he recognised as a new substance not hitherto described, and concludes "I hope I have demonstrated that the acid of fluor is and remains entirely a mineral acid *sui generis*."

The source of the silica which Scheele observed to be deposited when the acid vapours liberated by the action of sulphuric acid upon fluor-spar were dissolved in water was ascertained a few years later by Meyer† and by Wiegleb,‡ who showed that it was derived from the glass of the retorts which Scheele had used, and that it was not formed when the distillation was effected in metal vessels and when the acid vapours were dissolved in water contained in a leaden receiver. Meyer prefaces his paper§ with the following observations, which well deserve to be recalled: —

'It is always of advantage to chemistry when new and important experiments are controverted soon after their publication. If any mistakes, as so easily happens in chemical researches, be committed in the experiments themselves, or if a false theory be founded upon them, the error is not continued for half-a-century, nor does it pass from one elementary book into another till at last some sceptic thinks of inquiring more narrowly into the matter.

"If the experiments be exact, and the theory founded on them true, such a controversy commonly gives occasion to new researches which otherwise would not have been made, and the subject is placed in a clearer point of view.

"It were indeed to be wished that both parties held truth strictly in view; that they brought no false experiments into the dispute, and observed and explained the phenomena no otherwise than a friend to truth uninterested in the controversy would do, and advanced contradictory assertions with as much caution as possible. It is by no means rare for a man eager to convict his adversary of a mistake to commit another in the very same experiment by which he thinks to attain his purpose.

"Truth, however, let the dispute be carried on in whatever manner, is commonly a gainer, and this is no small advantage."

According to the ideas of Lavoisier, fluoric acid, as Scheele's acid of fluor was called in the new nomenclature, could only be a combination of oxygen with an unknown radical, and this was the first view put forward as to its nature. Lavoisier* himself writes regarding the supposed unknown radicals of muriatic, fluoric, and boracic acids:—

"No table has been made to show the result of combining these substances either with each other or with other combustible bodies, because they are all absolutely unknown. It is only known that these radicals are oxygenated, that they form muriatic, fluoric, and boracic acids, and that they are capable of entering into a great number of combinations, but chemistry has not yet been able to achieve their deoxidation, if one may use this expression."

And later, speaking of the investigations which had already been made on the subject of fluoric acid, he writes:—

"There only remains to-day to determine what is the nature of the fluoric radical, but as it does not appear that the decomposition of the acid has yet been achieved we can have no conception of it."

Gay-Lussac and Thenard† about this time tried to prepare fluoric acid pure in order to attempt the isolation of its radical, and read a paper on the subject before the Institute on January 23rd, 1809. They were able to prepare a tolerably pure concentrated acid, but it was still far from anhydrous. Their researches considerably increased our knowledge of the compound, and induced Ampère to put forward in a letter dated November 1st, 1810, addressed to Humphry Davy, the view that fluoric acid ought to be considered as a compound of hydrogen with a simple substance as yet unknown. In this letter he makes the following suggestion:—"It remains to be seen whether electricity would not decompose liquid hydrofluoric acid if water were removed as far as possible, hydrogen going to one side and oxyfluoric acid to the other, just as when water and hydromuriatic acid are decomposed by the same agent. The only difficulty to be feared is the combination of the oxyfluoric acid set free with the conductor with which it would be brought into contact in the nascent state. Perhaps there is no metal with which it would not combine, but supposing that oxyfluoric acid should, like oxymuriatic acid, be incapable of combining with carbon, this latter body might be a sufficiently good conductor for it to be used with success as such in this experiment."

In a second letter,‡ dated August 25th, 1812, Ampère suggested to Davy the name by which the element has ever since been known, "fluorine," in order to bring it into agreement with the recently adopted name chlorine.

Davy, accepting Ampère's views, made a number of experiments. At first he tried to show that hydrofluoric acid contained no oxygen, and subsequently enlarging the scope of his enquiry, endeavoured in various ways, including the one suggested by Ampère of electrolysing hydrofluoric acid, to isolate fluorine, but without success.

Davy§ states:—"I undertook the experiment of electrizing pure liquid fluoric acid with considerable interest, as it seemed to offer the most probable method of ascertaining its real nature, but considerable difficulties occurred in executing the process. The liquid fluoric acid immediately destroys glass and all animal and vegetable substances, it acts on all bodies containing metallic oxides, and I know of no substances which are not rapidly dissolved or decomposed by it, except metals, charcoal, phosphorus, sulphur, and certain combinations of chlorine. I attempted to make tubes of sulphur, of muriates of lead, and of copper containing metallic wires, by which it might be electrized, but without success. I succeeded, however, in boring a piece of horn

* "Untersoknung om Fluss-spath och dess Syra. Konigl. Swensk Vetenskaps Acad.," 1771, xxxiii., 120; Beddoe's Translation of Scheele's "Chemical Essays," Essays I. and II., London, 1786, pp. 1 and 27.

† "Baytraage zur Kenntniss des Fluss-spathsaure, Schriften der Berlinischer Gesellschaft Natur-forscher Freunde," Berlin, 1781, ii., 319.

‡ "Ueber Fluss-spathsaüre. Die neuesten Entdeckungen in der Chemie," von Dr. Lorenz Crell, Leipzig, 1781, i., 3

§ Printed among "The Chemical Essays of Scheele," Beddoe's translation, p. 49.

* "Traité élémentaire de Chimie," Paris.

† *Annales de Chimie*, 1809, [1], lxix., 204.

‡ "Letters of Ampère to Davy upon Fluorine," dated Paris, Nov. 1st, 1810, and August 25th, 1812; printed for the first time in *Annales de Chimie et de Physique*, 1885, [6], iv., 8.

§ *Phil. Trans.*, 1813, ciii., 270.

silver in such a manner that I was able to cement a platina wire into it, by means of a spirit lamp, and by inverting this in a tray of platina filled with liquid fluoric acid I contrived to submit the fluid to the agency of electricity in such a manner that in successive experiments it was possible to collect any elastic fluid that might be produced." He, however, obtained no results, except that the positive pole, which consisted of a platinum wire, became corroded rapidly and covered with a brown powder, while gaseous matter separated at the negative pole.

His next experiments were directed by the consideration that possibly the unknown element might be separated from the metallic elements combined with it either by chlorine or by oxygen. He continues, "In selecting compounds for experiments of this kind, I was guided by the relative attractions of the fluoric and muriatic acids, of chlorine, and oxygen. Horn silver and calomel, and muriate of potassa are not decomposed by fluoric acid, but fluate of silver, of mercury, and of potassa are easily decomposed by muriatic acid; I therefore conceived that the fluoric principle would most likely be expelled from the dry fluates of silver, mercury, and potassa by chlorine."

"The dry salts were introduced in small quantities into glass retorts, which were exhausted and then filled with pure chlorine; the part of the retort in contact with the salt was heated gradually till it became red. There was soon a strong action, the fluate of mercury was rapidly converted into corrosive sublimate, and the fluate of silver more slowly became horn silver. In both experiments there was a violent action upon the whole of the interior of the retort. On examining the results, it was found that in both instances there had been a considerable absorption of chlorine, and a production of silicated fluoric acid gas and oxygen gas. I tried similar experiments with similar results upon dry fluates of potassa and soda. By the action of a red-heat they were slowly converted into muriates with the absorption of chlorine, and the production of oxygen, and silicated fluoric acid gas, the retort being corroded even to its neck."

The obvious explanation of these phenomena is, that a particular principle, the acidifying matter of the fluoric acid, combined with the metals, is expelled from them by the stronger attraction of the chlorine, and that this principle coming in contact with glass decomposes it by its attraction for the silicum and sodium, and separates them from the oxygen with which they were combined. I made various attempts to procure the fluoric principle in a pure form. I heated the fluates of potassa and soda in trays of platina in a tube of platina connected with a vessel filled with chlorine. In this case the fluates were converted into muriates, with a considerable increase of the weight of the tray; and the platina was violently acted upon, and covered with a reddish brown powder; and in the instance in which fluate of potassa was used, a compound of fluate of platina and muriate of potassa was formed. There was considerable absorption of chlorine; but no new gaseous matter could be discovered in the gas in the tube.

Later, he somewhat more explicitly re-states Ampère's views as follows:—

"From the general tenor of the results that I have stated, it appears reasonable to conclude that there exists in the fluoric compounds a peculiar substance, possessed of strong attractions for metallic bodies and hydrogen, and which, combined with certain inflammable bodies, forms peculiar acids, and which, in consequence of its strong affinities and high decomposing agencies, it will be very difficult to examine in a pure form, and, for the sake of avoiding circumlocution, it may be denominated *fluorine*, a name suggested to me by M. Ampère."

Davy's difficulty in finding a material upon which the energetic principle of the fluorides would exert no action, led C. J. and Thomas Knox* to employ fluor-spar itself, this being easily worked and bearing exposure to a high temperature. Using fluor-spar vessels, they heated dry fluoride of mercury in chlorine, and later C. J. Knox* alone endeavoured to electrolyse hydrofluoric acid, which he thought to be anhydrous, employing a platinum wire as negative electrode and a piece of charcoal bound round with platinum wire as the positive electrode. In 1846 Louyet,† a Belgian chemist, also using a fluor-spar apparatus, tried the effect of chlorine on fluoride of mercury.

No results of importance were obtained by these chemists, as the materials they used were not free from water.

Gay-Lussac and Thenard, Davy, and the brothers Knox had all been made seriously ill by accidentally breathing the vapour of hydrofluoric acid, not one of them having taken sufficient precautions to prevent its escape into the air of the laboratory, while Louyet and Nickles‡ actually lost their lives from the same cause.

* *London and Edinburgh Phil. Mag.*, 1836, ix., 107.

VOLTAIC CELLS CONTAINING THE SAME SALT DISSOLVED IN TWO DIFFERENT SOLVENTS.§

By Principal A. P. LAURIE, M.A., D.Sc.

IF a salt is shaken up with two different liquids which do not mix, and in both of which the salt is soluble, the salt is shared between the two liquids in a definite proportion.

For dilute solutions this proportion remains the same, and the ratio is known as the partition coefficient.

If after shaking up together the liquids are allowed to separate from each other and two similar electrodes are introduced, there will be no E.M.F. between the electrodes.

The particular case, to take an example, of water, ether, zinc sulphate with zinc electrodes, was investigated by Luther (*Zeit. Phys. Chem.*, 1896, xix., p. 567.

The mathematical investigation of such cells was undertaken by Abel (*Zeit. Phys. Chem.*, 1906, lvi., p. 612), and the following is the simplest statement of the condition of equilibrium in such a cell:—

Let P_w and P_s be the solution pressures of the metal in the two solvents w and s, and let $\bar{c}_w$ and $\bar{c}_s$ be the ionic concentration of the metallic ions in the two solvents after they have been shaken up together.

Then we have—

$$E = RT\left(\log \frac{P_w}{\bar{c}_w} - \log \frac{P_s}{\bar{c}_s}\right) = 0.$$

If some different concentration of the salt be taken, then at the boundary of contact the concentrations will be $\bar{c}_w$ and $\bar{c}_s$ respectively, and therefore each section of the cell can be regarded as an ordinary concentration cell, with the concentration changing from C_w to $\bar{c}_w$, and from C_s to $\bar{c}_s$ respectively.

If the v_w and u_w and v_s and u_s are the ionic velocities in the two solutions, the expression for the E.M.F. becomes—

$$E = \frac{2v_w}{u_w + v_w}\,\frac{RT}{m}\,.\log.\frac{C_w}{\bar{c}_w} - \frac{2v_s}{u_s + v_s}\,\frac{RT}{m}.\log\frac{C_s}{\bar{c}_s}\,.$$

If instead of two liquids which do not mix we select two liquids which do mix, the problem is complicated by their mixing at the boundary, and so forming intermediate solvents, and therefore for their proper investigation we must imagine them separated by a third solvent which mixes with neither, but the different solubilities of the salt in each liquid will produce an E.M.F., and enable us to determine therefore the partition ratio electrically.

* *London and Edinburgh Phil. Mag.*, 1840, xvi., 199.

† "Nouvelles recherches sur l'isolement du fluor," *Comptes Rendus*, 1846, xxiii., 960; and "De la véritable nature de l'acide fluorhydrique," *Comptes Rendus*, 1847, xxiv., 434.

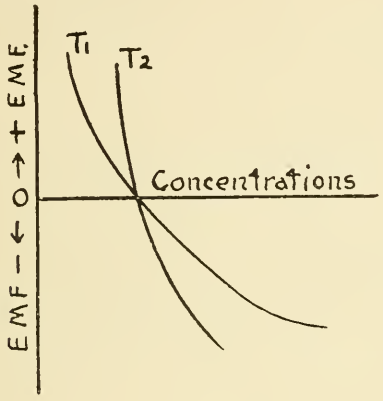
‡ *Moniteur Belge*, April 14, 1869.

§ A Lecture delivered before the Faraday Society, December 10, 1912.

In order to investigate these cells I used little stoppered vessels inverted and plunged in the solution, and a Dolazelek electrometer. Such stoppers, if not greased, form a sufficient electrical connection, while preventing mixing (*Proc. Roy. Soc. Edin.*, 1911, vol. xxxi., Part III., p. 387). The cells I used consisted of potassium iodide and iodine dissolved in water and nitrobenzene, with platinum electrodes; potassium iodide and iodine dissolved in water and ethyl alcohol, with platinum electrodes; and potassium iodide in water and ethyl alcohol with silver, silver iodide electrodes.

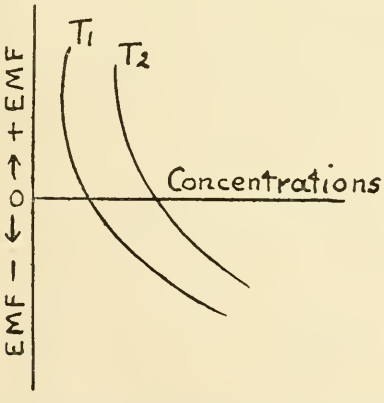
My first experiments were with the view of testing the effect of temperature on the cells.

If we plot concentration against E.M.F. for two different temperatures in ordinary concentration cells, keeping the concentration the same on one side and changing it on the other, then the curves obtained are of the following form :—



The curves cross at zero E.M.F., and with the reversal of the E.M.F. the temperature coefficient is reversed, the cells being always endothermic and the temperature coefficient + -ive.

In the cells under discussion the curves are of the following form :—



With the reversal of the E.M.F. the temperature coefficient is not reversed, the cell becoming exothermic and giving out heat as well as producing an electric current.

If we take the case of potassium iodide in water and alcohol the cell is exothermic when the current is in the direction of transferring potassium iodide from water to alcohol, the ratio of about 1 to 20 being the concentration of no E.M.F.

If a cell is constructed which has no E.M.F. at T_1, then on raising the temperature to T_2 a current flows in the direction to transfer potassium iodide from alcohol to water, and the cell is endothermic.

On now cooling to T° the current is reversed and the cell is exothermic, the potassium iodide being re-transferred from water to alcohol, the whole forming a very neat heat engine.

It is evident that if the rate of change of solubility of the salt with temperature was the same in both solutions, then on raising or lowering the temperature no E.M.F. would be produced.

Experiments proving these conditions of E.M.F. with temperature were made with the three types of cell already described.

In iodine, potassium iodide, alcohol, water cells with 0·025 molecule of potassium iodide on each side the equilibrium for iodine is 0·0138 molecule in water against 0·086 molecule in alcohol.

The next problem is to find the source of energy in these cells which makes it possible for them to be exothermic.

To take the case of potassium iodide in water and alcohol, or any other convenient solvent, it is evident that during the passage of a given current a molecule of potassium iodide is transferred from the one solution to the other. As without the ionic transfer numbers for both solvents we cannot define what the amount of this current will be, we shall, so as to simplify our equations, define as unit current the amount required to effect this transference of one molecule.

During this transference a molecule of the salt is removed from the one solvent and dissolved in the other. If λ' is the latent heat of solution of 1 grm. molecule of potassium iodide in water (calling heat absorbed + -ive), and λ the latent heat of solution of an equal quantity in alcohol, then when the salt is transfered from alcohol to water—

$$E = \lambda' - \lambda + T\frac{de}{dT} \quad . \quad . \quad . \quad . \quad . \quad . \quad (1).$$

As heat is absorbed when potassium iodide is dissolved, then if λ' is greater than λ, heat is absorbed in the cell during the change, and the cell is endothermic. If, however, the concentrations are so arranged as to transfer the salt from water to alcohol, then the equation becomes—

$$E = \lambda - \lambda' + T\frac{de}{dT} \quad . \quad . \quad . \quad . \quad . \quad . \quad (2),$$

and the cell is exothermic.

For equation (1) $T\frac{de}{dT}$ has a + -ive value, the E.M.F. rising with increase of temperature, and for equation (2) $T\frac{de}{dT}$ is − -ive.

Starting from saturated solutions which are necessarily in equilibrium for solvents which do not mix, and applying van't Hoff's equation for latent heats, exactly the same result is arrived at, the change of E.M.F. with change of temperature—

$$de = (\lambda' - \lambda)\frac{T_2 - T_1}{T_1}\ ;\ \text{that is, } \lambda' - \lambda = T\frac{de}{Td} \quad . \quad . \quad (3).$$

It is evident that if the transfer numbers are also known these equations enable us to measure the differences between the latent heats of solution in very dilute solutions of a salt in two different solvents.

So far we have considered the alcohol as behaving like a solvent that does not mix with water. It remains to be seen how far this view must be modified, and to describe the particular case of water alcohol-potassium iodide cells with silver, silver iodide electrodes.

The result of the E.M.F. measurements is to show that these cells are in equilibrium when the solutions are in the ratio of 1 molecule of potassium iodide in alcohol to 20 molecules of potassium iodide in water.

Now the solubility of potassium iodide in alcohol is 0·096, while in water it is 6·2, so that if the results are correct equilibrium would not exist when both solvents were saturated.

Experiments with a saturated solution of potassium iodide in alcohol against saturated and strong solutions of potassium iodide in water confirm this.

When the water solution is saturated there is an E.M.F. transferring potassium iodide from water to alcohol, and the equilibrium E.M.F. is only reached when the water solution has been diluted to the strength of about 2 molecules to 1000 cc., thus confirming the former results.

If alcohol is added to a strong solution of potassium iodide in water, the potassium iodide is partially precipitated. It seemed therefore necessary to investigate the limits of this precipitation by adding alcohol in large excess, already saturated with potassium iodide, to water solutions of potassium iodide.

The result of these experiments was to show that the potassium iodide is precipitated until the water content is reduced to 2·1 molecules per 1000 cc.; that consequently if a saturated solution of potassium iodide in alcohol is in contact with a 2·1 molecule solution in water no precipitation will take place, but all stronger solutions are precipitated until this dilution is reached. We arrive, therefore, at a modified definition of the partition coefficient between two liquids which inter-diffuse, and of which one is able to partly precipitate salt out of the other.

Two such solutions are in partition equilibrium when the ratio of the strength of solution is such that when the weaker solvent is saturated the stronger solvent is sufficiently diluted to prevent any precipitation of salt by inter-diffusion.

In the case of water, alcohol, and potassium iodide, this ratio is 1 to 20 instead of 1 to 60, the ratio of saturation.

There still remains the interesting question of the source of energy in such a cell when the salt is saturated on both sides and yet the cell is exothermic. I suggest that it is due to the heat set free by the ionic mixing of water and alcohol, due to the carriage of water and alcohol across the boundaries combined with the respective ions.

Much further investigation, however, would be necessary to test this hypothesis, and, to sum up, I only claim here to have established the relationship between the latent heats of solution and the E.M.F.'s of such cells, and to have shown the condition of equilibrium for mutually diffusing solvents, when one solvent tends to precipitate from solution the salt in the other.

The full details will be found in the paper in the *Proceedings of the Royal Society of Edinburgh*, vol. xxxi., Part III., No. 24, p. 375, already referred to.

MONEL METAL.*

By RICHARD H. GAINES.

History.

About seven years ago one of the large smelting companies began investigating the chemical and physical properties of an alloy that had been reduced directly from a nickel-copper matte, without the previous separation of the two metals. This alloy was found to possess not only the more valuable properties of nickel, but other desirable properties in addition, that would ensure a wide usefulness, and owing to the simple method of production, was obtainable at about one-third the cost of nickel. The alloy consists primarily of nickel and copper in the proportion of 3 parts of nickel to 1 part of copper, this being the proportion in which the two metals are found together in nature in the great deposits of nickel ore at Copper Cliff in Canada.

The old Swedish and German miners supposed the mineral küpfernickel to be a counterfeit or base ore of copper. A fuller knowledge of nickel led to its being better appreciated, as it is now worth nearly three times as much as copper.

Nickel and copper are associated in enormous pyrrhotite deposits in the Sudbury district of Ontario, Canada, and one of the most difficult problems in the treatment of these ores has been that of separating the two metals. In 1905-6, the International Nickel Company, considering, no doubt, that for many purposes there was no need to separate the amicable metals nickel and copper, took up the problem of reducing them together and obtaining an alloy of the two metals in the proportions in which they occur in the ore. The method adopted consists merely in eliminating the impurities, except a small percentage of reduced iron and a minor quantity of other substances which remain with the alloy.

Process of Manufacture.

Synopsis.—The ore from the mines is first reduced to a matte, which is blown until the iron is nearly eliminated, the sulphur is removed by roasting, and the combined oxides remaining are reduced to metal.

The general method of production includes roasting the ore in heaps, followed by smelting in a blast furnace, and further enriching in a converter, which yields a high-grade matte containing about 80 per cent nickel and copper, from 1—2 per cent iron, and the rest sulphur. By careful attention to the furnace charge, it now is claimed that a Bessemer matte can be produced within 1 per cent of the required proportion. The rich matte is shipped to the Orford refinery, where it is ground and roasted in hand rabbled reverberatory furnaces to remove the sulphur, carbonate of soda being used to finish the elimination of the sulphur. The product should be oxides of nickel and copper, with a small proportion of iron, and only a trace of sulphur. This is charged with charcoal into a reverberatory melting furnace fired with oil. The nickel and copper oxides are thus reduced to metal, and melted.

The alloy thus obtained was found to possess such valuable properties as would ensure it a very wide use on its own account. It was named Monel metal after Mr. Ambrose Monel, the President of the International Nickel Company.

Composition.

The ores of the Sudbury district vary both in the amount and proportion of nickel and copper, and therefore the proportions of these two metals in the alloy will vary within certain limits with the composition of the ore treated. The ore from which the Monel metal is derived contains generally about 4·85 per cent of nickel to about 1·75 per cent copper. When this ore, as it occurs in nature, is reduced to metal, the resulting alloy contains from 66—70 per cent nickel, from 23—28 per cent copper, and from 3—5 per cent of other metals, including iron, and a small proportion of manganese.

C. F. Burgess and James Aston (*Metallurgical and Chem. Eng.*, viii., 452) give the following analysis of a sample of Monel metal examined in 1909:—

	Per cent.
Nickel	67·96
Copper	26·00
Iron	2·80
Manganese	1·62

Analyses of Monel metal quoted by A. Stansfield, C.E. (Canadian Society of Civil Engineers, *Transactions*, 1909, xxiii., 302—309) are as follows:—

	Cast bar.	Rolled bar.
Nickel	68·90	67·55
Copper	26·55	26·25
Iron	3·30	3·25

On looking through the literature of the subject, no very recent analyses were found. The analyses of cast, rolled,

* From the *Journal of Industrial and Engineering Chemistry*, iv., No. 5.

Analyses of Cast Monel Metal.

(Samples taken at the Foundry of the Bayonne Casting Co., Bayonne, N.J.).

Lab. No.	Description.	Copper.	Carbon.	Iron.	Nickel.	Silicon.	Manganese.	Cobalt.	Total.
		Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
1146	Heat 301	26·59	0·27	3·19	68·22	1·10	0·26	Trace	99·63
1147	Heat 307	27·02	0·31	2·40	68·49	1·08	0·49	Trace	99·79
1148	Heat 308	26·59	0·43	2·87	68·23	1·24	0·44	Trace	99·80
1149	Heat 312	27·04	0·39	2·68	68·10	1·17	0·37	Trace	99·75
1150	Heat 315	27·27	0·39	2·40	68·50	1·23	0·09		99.88
1151	Heat 318	26·81	0·38	2·54	68·30	1·36	0·23		99·62
1152	Heat 329	27·53	0·31	2·16	68·28	1·41	0·14		99·83
1153	Heat 335	27·38	0·25	3·33	68 46	1·24	0·11		99·77

Analyses of Rolled Monel Metal.

(Samples taken at the Foundry of the Bayonne Casting Co., Bayonne, N.J.).

1154, No. 1	Test 275	26·57	0·28	2 09	69·04	0·16	1·32	Trace	99·46
1155, No. 2	Test 275	26·71	0·44	2·11	68·81	0·17	1·35	Trace	99·59
1156, No. 4	Test 275	26·99	0·37	2·07	68·89	0·18	1·26	Trace	99·76
1157, No. 6	Test 275	24·76	0·33	2·44	69·83	0·37	1·82	Trace	99·55
1158, No. 7	Test 275	26·94	0·39	2·16	68·48	0·12	1·54	Trace	99·63
1159, No. 8	Test 275	26·21	0·43	2·41	68·63	0·20	1·73	Trace	99·61

Analyses of Forged Monel Metal.

(Samples submitted by the Bayonne Casting Co., April 6, 1911).

1021	Specimen taken midway between centre and outside of billet ..	26 69	0·19	2·13	69·45	—	1·38	—	99·84
1022	Specimen from centre of billet .	26·78	0·17	2·14	69·52	—	1·50	—	100·11
1023	Specimen from outside of billet .	26·83	0·18	2 19	69·54	—	1·48	—	100·22

and forged metal (given in accompanying table) were made at the Laboratory of the Board of Water Supply, New York City, during the latter half of 1911.

For such a material as Monel metal, which is not a pure alloy, the feature of these analyses is the remarkable approach to uniformity in composition. If compared with the earlier published analyses, it would appear that the manufacturers have perfected the methods of reduction from ore and matte to such a degree as nearly to control the composition. In the present process of manufacture, the claim is made that the physical properties of Monel metal are not materially affected within the limits of variation in which the constituents occur. If this is true, a closer uniformity in the results of physical tests must be looked for from improvements in the heat treatment. As a matter of fact, the effect of variation in the copper-nickel ratio, as well as the influences of the presence of varying amounts of carbon, iron, silicon, and manganese, have not hitherto been studied, and are, therefore, not yet understood. A comparison of the chemical analyses with the physical tests made at the laboratory affords some deductions.

Nickel-Copper Ratio.

On looking over the results of the physical tests, it would seem that the variations found bear little relation to the chemical composition. Specimens of the cast metal in which the nickel-copper ratio was about the same, and other constituents in close agreement, gave a considerable difference in strength and yield point. For example, the specimen from heat 307 showed an ultimate strength of 69,100, and elastic limit 38,450, with a nickel - copper ratio of 68·49—27·02, while the specimen from heat 312 with a nickel-copper ratio of 68·10—27·04, and other constituents nearly identical, gave an ultimate strength of 73.750, and elastic limit 44,550. The difference of 10 per cent in ultimate strength and 15 per cent in elastic limit here is plainly due to some other cause than composition.

Carbon.

In accordance with previous examinations of this material, only the total carbon was determined in the samples submitted. With respect to the influence of this element, test 275, No. 1, gave ultimate strength 85,250, yield 51,250, and carbon 0·28. Same test, No. 2, showed ultimate strength 86,200, yield 58,250, and carbon 0·44 with other chemical constituents agreeing closely. Same test, No. 4, representing only a different section from the same rod, gave ultimate strength 85,500, yield 51,300, with carbon 0·37. The ultimate strength and yield in these three cases appear to follow in some measure the carbon content. In future study of Monel metal, it would be well to ascertain the carbon relations, for unless it is known in what form the carbon exists in the metal (whether free or combined, and in what ratio), it is fruitless to attempt deductions.

Iron.

Generally speaking, iron hardens, whitens, and increases the strength of Monel metal, but reduces the elastic limit. In the tests on the cast metal, heat 301, with an iron content of 3·19 per cent, showed ultimate strength 71,600 and elastic limit 39,600. In heat 315, where the iron was 2·40 per cent, the ultimate strength was 66,800 and the elastic limit 46,950. In the rolled metal where the iron is high, the tensile strength is high, but with these tests the limit of elasticity does not appear to follow any rule.

Silicon and Manganese.

In the narrow limits of variation in which these metals were found, no indication was observed of any material effect on physical properties. Manganese is an advantage as a deoxidiser, and it serves a useful purpose in rendering harmless any sulphur that might be present, forming as it would manganese sulphide.

The results of the analyses in general show that the chemical composition alone is an insufficient guide to the strength or other physical properties of Monel metal, which depend, as in steel, so largely upon other influences, and especially heat treatment. Much light on these could be obtained from investigation with the microscope. A metallographic examination of the structure of the various specimens under test would be of great assistance in revealing segregation, the form in which the carbon is present, and other facts having an important bearing on the physical and chemical constitution of the metal.

While the laws governing the nickel-copper alloys are not thoroughly understood, some progress has been made in this study. There are no chemical compounds of copper and nickel, neither is there any eutectic mixture. The

metals unite in all proportions without any separation on cooling. Hence, it is inferred that the two metals form solid solutions or mixed crystals in all proportions.

Working with pure metals, Hiorns ("Copper-Nickel Alloys," *Metal Industry*, Aug. and Sept., 1911) found that nickel dissolves in copper up to a certain percentage forming homogeneous solid solutions, and, on the other hand, taking nickel as the solvent, copper dissolves in nickel, forming homogeneous solid solutions up to a certain limit. These two solutions are miscible in all proportions. These facts have a direct bearing on observations made by David H. Browne, Metallurgist of the Canadian Copper Company (*Mining World*, xxx., 470), after five years' study of copper matte and copper nickel matte in the Bessemer converter, and in the manufacture of Monel metal. He submits the following conclusions :—

1. Nickel-copper alloys act in the matte-blow like one metal.

2. Nickel-copper alloys follow during the matte-blow exactly the same laws that govern the behaviour of copper alone.

Browne presents much data to prove that copper-nickel alloys form, as far as conversion is concerned, one homogeneous metal. In conversion, copper and nickel act together, presenting the same curious resistance to oxidation, and their relations toward iron are exactly similar to the relations of copper alone. The resistance to oxidation in the converter may be in some way connected with the resistance of the finished Monel metal to oxidation and corrosion. These facts seem to suggest the idea that the metal is an entity by itself.

As the component metals have never been separated from each other, the particles of each seem to be in more intimate contact than can be attained by any synthetic method of manufacture. It is claimed that melting the constituent metals together has produced no alloy having the same physical properties as the Monel metal obtained direct from the matte. The metal must therefore owe some of its remarkable properties to the grouping of its constituents. Small quantities of foreign substances which ordinarily affect the structure of alloys in general may be of negligible effect in an alloy of this type.

In certain of its chemical as well as physical properties, Monel metal closely resembles nickel. It is slowly dissolved by hydrochloric acid and by sulphuric acid, but dissolves rapidly in nitric acid with the evolution of nitric oxide. It is apparently unaffected by alkalis, and shows the same stability as nickel in the presence of other corrosive chemicals. Like both nickel and iron, Monel metal is magnetic, a property which it loses above a certain temperature. Like nickel and iron it absorbs carbon, and like steel its physical properties are profoundly influenced, not only by the percentage of carbon, but the form in which it exists in the metal.

In the examination of Monel metal at the laboratory, the carbon present was observed in some samples in the free form as graphite, and in a smaller degree as combined carbon, the differential relations apparently depending as in iron on the rate of cooling.

(To be continued)

American Philosophical Society.—The annual general meeting of this society will be held at Philadelphia on April 17th, 18th, and 19th, 1913, beginning at 2 p.m. on Wednesday, April 17th. Members desiring to present papers are requested to send to the Secretaries, at as early a date as practicable and before March 5th, 1913, the titles of these papers, so that they may be announced on the preliminary programme which will be issued immediately after that date, and which will give in detail the arrangements for the meeting. Papers in any department of science come within the scope of the society, which, as its name indicates, embraces the whole field of useful knowledge.

RARE EARTH REACTIONS IN NON-AQUEOUS SOLVENTS.*

By O. L. BARNEBEY.

(Continued from p. 267).

3. The Basic Nitrate Separation Using Acetone as the Medium of Extraction.

When a solution mixture of rare earth nitrates is evaporated to dryness and extracted with acetone, complete solution is seldom effected, a residue remaining in almost every instance. If the nitrates are heated after evaporation the amount of insoluble residue is increased until by moderately strong ignition the entire mass is converted to insoluble basic nitrate or oxide. This deportment of the nitrites is made use of in the well-known aqueous basic nitrate schemes of fractionation, and was tried using acetone instead of water for extraction.

Series I. *and* II.

Thirty grms. of yttrium earth oxides containing a very slight trace of didymium were dissolved in nitric acid and evaporated to dryness on the steam-bath. The resulting nitrates were treated with acetone, the whole transferred to a flask and shaken until the residue was very finely divided and the extraction apparently complete. In no case was filtration made unless the residue had remained in contact with the acetone for two hours. The residue was filtered off, washed several times with acetone, and converted to the oxide. Conversion to oxide by direct ignition gave some difficulty due to the tendency to fuse and not go to a dry powder. Hence the residue in each case was dissolved in nitric acid, the earths precipitated by oxalic acid from a dilute solution which was slightly acid, and after filtration ignited to oxide. The washings and filtrate of the first extraction were evaporated to a stiff consistency with thorough stirring at the last, thus giving a slight amount of decomposition in as uniform a manner as possible and avoiding local decomposition. The residue was again extracted as before, &c. The ignited oxides were labelled in order 1, 2, 3, &c.

Examination of the resulting fractions showed rather inconsistent results. The conclusion was drawn that the heating was not regulated in a sufficiently uniform manner to insure good fractionation, and a second series of fractions was obtained with this in mind. Although the fractions were more uniform in size, spectroscopic examinations and determinations of atomic weights did not show uniform results. From this it was concluded that the nitrates were not heated to a sufficiently high temperature.

Series III.

Yttrium earth material which originally came from fergusonite was employed. In this case decomposition was carried much further preceding extraction with acetone. Heating was continued with constant stirring, using a heavy rod and casserole, until the material was hard and in small lumps. The mass thus treated tends to swell up as decomposition proceeds, but with a little care in stirring the mass can be kept fairly uniform and local decomposition avoided for the most part. The lumpy material is pulverised before acetone is added for extraction. One small and three larger fractions were obtained.

Fractions.	Quantity. Grms.	Colour of oxide.	Equivalent weight.
1.	0·3	Yellow	Not determined, at least 75 per cent CeO_2
2.	4·0	Almost white, very slightly pink	115·8
3.	3·5	Almost white, yellow tinge	106·5
4.	3·0	Chamois	103·3

* *Journal of the American Chemical Society*, xxxiv., No, 9.

Spectroscopic Examination.

Fraction 1 not examined.

Fraction 2 :—

			Comparative intensity.
(*a*) 653 / 650	Erbium	Moderately strong	2
(*b*) 642 / 641	Holmium	Very light band	1
(*c*) 582 / 576	Didymium	Very light band	0·5
(*d*) 540 / 538	Erbium	Well defined	2
(*e*) 537 / 535	Holmium	Well defined	1·5
(*f*) 523 / 517	Erbium	Very heavy and well defined.	10
(*g*) 487 / 484	Erbium-Holmium	Moderate	2
(*h*) 449 / 446	Dysprosium	Very heavy line	9

Fraction 3 :—

Same lines as above only much weaker. (*c*) Heavier.

Fraction 4 :—

(*a*), (*b*), (*e*), (*d*), and (*g*) completely gone. (*c*) Much heavier.

(*f*) Is a moderately light band with an intensity of about 2.

(*h*) Is a moderately light band with an intensity of about 2.

572 / 570 Neodymium. A light band. Intensity about 1.

This examination shows a concentration of erbium, holmium, and dysprosium in the first fractions and didymium in the last. Cerium comes out before the members of the yttrium group. The equivalent weight determinations show a concentration of yttrium in the last fractions.

Series IV.

The fractions from Series II. were united and refractionated in a manner similar to Series III., with the following results :—

Fraction.	Colour of oxide.	Equivalent wt.
1.	Very light buff (slightly pink)	115·2
2.	Much lighter than 1	110·3
3.	Somewhat darker yellow than 2	109·3
4.	Chamois	107·0

Spectroscopic Examination.

			Intensity.
(*a*) 654 / 650	Erbium	Light band.	1·5
(*b*) 641 / 639	Holmium	Moderate	2·5
(*c*) 536 / 534	Holmium	Moderate	2
(*d*) 523 / 517	Erbium	Moderate	2·5
(*e*) 486 / 484	Erbium-Holmium	Light	1
(*f*) 460 / 456	Dysprosium	Heavy	7

Fraction 2 :—

(*d*), (*f*), (*e*), and (*c*) lighter.

Fraction 3 :—

Very light line just discernible at 580-didymium. Line (*b*) about the same intensity as in 2, but other lines much lighter.

Fraction 4 :—

578 / 580 Didymium. Moderately strong. Intensity about 2.

It has become the strongest band of the field except (*f*), which has now an intensity of about 5. Other lines are weak.

This series corroborates the results of Series III.

Conclusions.

The use of acetone as a medium of extraction in the basic nitrate fractionation of the members of the yttrium group works satisfactorily, and can be employed for the purification of some of the members of this group. Erbium, holmium, and dysprosium are thrown out in the first fractions and the yttrium last. Any cerium which may be present is concentrated in the first fraction, and didymium in the last with the yttrium. In fact, the concentration of cerium in the first fraction is so marked that cerium can be obtained very quickly in a high degree of purity with this method, starting with crude rare earth mixtures. The fact that didymium is concentrated toward the last is also worthy of especial mention inasmuch as cerium concentrates in the first fraction.

(To be continued).

SIR HENRY ROSCOE'S EIGHTIETH BIRTHDAY.

THE Right Hon. Sir Henry Roscoe celebrated his 80th birthday on Tuesday, January 7th, at his country house, Woodcote Lodge, West Horsley.

His former students and friends having decided to commemorate the occasion by the presentation of his bust to the Chemical Society of London as a tribute of appreciation of his long life and work, a representative deputation visited Sir Henry to convey to him the congratulations of his former students and to acquaint him with their proposal for the commemoration of his birthday. The deputation consisted of Sir Edward Thorpe, C.B., F.R.S., who acted as Chairman, Prof. Smithells, F.R.S., Prof. Bedson, Dr. Charles A. Keane, Prof. Harden, F.R.S., Prof. Crossley, F.R.S., Mr. E. J. Bevan, and Mr. Watson Smith.

A congratulatory address was presented, in which reference was made to Sir Henry's continued and successful services to Chemistry and to the large debt of thanks that was owed to him by his Pupils, his Science, and his Country. It was pointed out that, although it was twenty-seven years since he resigned the Chair of Chemistry at Owen's College, his influence as their teacher and friend had continued, and that amongst his former pupils there were many who, thanks to the teaching they had received at his hands, had been enabled to contribute to the advancement of Science, and who in their turn, both in academic work and in industry, had been privileged to train a second generation of men, whose labours it was hoped would add further testimony to the value of his guidance and example.

Sir Henry Roscoe, in acknowledging the address, expressed his gratitude to his former students who had sought this opportunity to recall his long association with them as their teacher and friend, and said there was no honour he would value more than their proposed form of commemorating his 80th birthday. His aim throughout his life had always been to do all in his power for the furtherance of Chemical Science and to help and encourage those who came to him as students and fellow-workers. This, he felt, was the only claim he had to their welcome and valued tribute of affection and gratitude,

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, December 19th, 1912.

Prof. PERCY F. FRANKLAND, LL.D., F.R.S., President, in the Chair.

MESSRS. Ridsdale Ellis, E. L. Lomax, C. E. Sladden, John W. Patterson, and E. A. Cooper were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. John Hugh Christie, B.Sc., care of Dr. Bean, Cross Gates, Leeds; Roland Doumin, 76, Tannsfield Road, Sydenham, S.E.; Albert Edward Garrett, B.Sc., Yaverland, Clarence Road, St. Albans; Douglas Henville, 67, Glencoe Street, Newington, Hull; Thomas James Kirkland, B.Sc., Hereward Hall, Ely; William Norman Rae, B.A., Royal College, Colombo, Ceylon; Hermann Horace Roskin, B.Sc., 11, Newlands Road, Middlesbrough; William Slessor Simpson, M.A., B.Sc., Dynamite Factory, Somerset West, S. Africa.

Of the following papers, those marked * were read :—

*321. "*A Qualitative Attempt to Harmonise the Relation between Temperature and Rotation for Light of all Refrangibilities of Certain Active Substances, both in the Homogeneous State and in Solution.*" By THOMAS STEWART PATTERSON.

Evidence was adduced to show that the temperature-rotation curve for an active substance is probably irregularly periodic, and that in comparing the rotation values for different substances of a similar class account should be taken of something corresponding with phase and something corresponding with amplitude. The influence of a solvent appears to be to shift the temperature-rotation curve as a whole towards a lower or higher temperature with corresponding difference in amplitude. The maximum rotation occurs at slightly different temperatures for light of different refrangibilities, and this accounts for the phenomenon of anomalous rotation-dispersion. The influence of solvents on anomalous rotation-dispersion appears to be just the same as on the temperature of maximum rotation. The recognition of the variation of the temperature of maximum rotation appears to bring into one general scheme all the diverse phenomena of optical activity.

DISCUSSION.

The PRESIDENT said that in all the six cases in which he himself had found a maximum rotation—(ethyl dibenzoyltrartrate, ethyl and methyl di-*o*-toluoyltartrates, methyl di-*o*-chloro-, di *o*-bromo-, and di-*o*-iodo-tartrates)—the latter occurred at a temperature below the melting point of the substance. He suggested that the maximum in such cases might be associated with the complex condition of the liquid in the supercooled state in which two or more different kinds of molecules might be present. Some of the maxima recorded by Dr. Patterson appeared to him to have been obtained at temperatures so high that some decomposition might be feared, but he presumed that the author had taken the possibility of a spurious maximum being thus obtained into consideration.

In reply to the President, Dr. PATTERSON stated that the maxima observed in the temperature-rotation curves was not due in any way to decomposition of the substances on heating. In cooling from a high temperature the rotation was observed to rise and then diminish again.

*322. "*The Photography of Absorption Spectra.*" By THOMAS RALPH MERTON.

The photographic methods generally used for the observation of absorption spectra are not suitable for quantitative investigations owing to the complicated conditions which govern the density of a photographic plate.

A photographic method has been found for the determination of extinction curves which is free from these objections.

*323. "*The Constitution of Ortho-diazoimines.* Part II. *The* p-*Tolylnaphthatriazoles.*" By GILBERT T. MORGAN and FRANCES MARY GORE MICKLETHWAIT.

In continuation of earlier experiments (*Proc.*, 1910, xxvi., 151), attempts have been made to prepare the third isomeride, having the general formula $\alpha\beta$-$C_{10}H_6{:}N_3{\cdot}C_7H_7(p)$.

2 : 4-*Dinitro*-1-p-*tolyl*-α-*naphthylamine* (yellow needles, m. p. 196—198°), obtained by boiling 1-chloro-2 : 4-dinitronaphthalene and *p*-toluidine in xylene solution, yielded on complete reduction the somewhat oxidisable base 1-p-*tolyl*-1 : 2 : 4-*triaminonaphthalene* (colourless needles, m. p. 177°). The action of nitrous acid on this triamine is remarkable, as it leads to the elimination of *p*-toluidine, in the form of *p*-toluenediazonium chloride, and to the production of 2-amino-1 : 4-naphthaquinoneimide, a compound hitherto obtained by the action of ferric chloride on 2 : 4-diamino-α-naphthol. The partial reduction of 2 : 4-dinitro-1-*p*-tolyl-α-naphthylamine is under investigation.

*324. "*Co-ordination Compounds of Vanadium.* Part I. *The Acylacetonates.*" By GILBERT T. MORGAN and HENRY WEBSTER MOSS.

Vanadium terbenzoylacetonate,

$$V\left[\begin{matrix}O{=}C(CH_3)\\ O\cdot C(C_6H_5)\end{matrix}\!\!>\!\!CH\right]_3,$$

dark chocolate-brown leaflets, m. p. 218—220°, was obtained by the interaction of anhydrous vanadium trichloride, benzoylacetone, and alcoholic sodium ethoxide; it is insoluble in water, and dissolves freely in chloroform or benzene. In the moist condition it oxidises to the emerald-green *vanadium oxybisbenzoylacetonate* (*vanadyl bisbenzoylacetonate*),

$$VO\left[\begin{matrix}O:C(C_6H_5)\\ O-C(CH_3)\end{matrix}\!\!>\!\!CH\right]_2,$$

which is more readily prepared by dissolving freshly precipitated vanadyl hydroxide in an alcoholic solution of benzoylacetone.

Vanadium oxybisacetylmethylacetonate (*vanadyl bisacetylmethylacetonate*),

$$VO\left[\begin{matrix}O{:}C(CH_3)\\ O{:}C(CH_3)\end{matrix}\!\!>\!\!C{\cdot}CH_3\right]_2,$$

sage-green, acicular prisms, results from the interaction of vanadyl hydroxide and alcoholic acetylmethylacetone.

The ultra-violet absorption spectra of the vanadium teracylacetonates and vanadium oxybisacylacetonates in alcoholic solution differ from those of vanadium trichloride and vanadyl dichloride in showing persistent absorption bands like the bands exhibited by the acylacetones themselves, whereas the two chlorides indicate only general absorption in dilute solutions.

325. "*Dibenzyl- and Diphenyl-silicols and -silicones.*" By GEOFFREY MARTIN.

The author, by means of a tabular comparison between the compounds recently described by Kipping (*Trans.*, 1912, ci., 2108 *et seq.*) and the same ones previously described by himself (*Ber.*, 1912, xlv., 403), controverted Kipping's statement (*loc. cit.*) that an erroneous account has been given of these compounds. The author pointed out that he had not described any "isomeric" diphenylsilicols in his paper (*loc. cit.*), as asserted by Kipping, and stated that Kipping had merely "rediscovered" the two modifications of diphenylsllicol described by him ten months previously (*loc. cit.*). The author maintained the correctness of his conclusion that one modification can pass into the other, and vice versa. He pointed out that Kipping himself records the passage of one modification into the other, and actually states that it is a result "which appears to be fully established" (*loc. cit.*, p. 2124))

326. "*Optically Active Glycols Derived from the Phenyllactic Acids.*" (Part I.). By ALEX. MCKENZIE and GEOFFREY MARTIN.

The authors have prepared and examined a number of

glycols derived from esters of β hydroxy-β phenylpropionic acid and α-hydroxy-β-phenylpropionic acid respectively by the application of Grignard reagents.

327. "*Diphenylene.*" (Part II.). By James Johnston Dobbie, John Jacob Fox, and Arthur Josiah Hoffmeister Gauge.

Certain derivatives o diphenylene, $C_6H_4{:}C_6H_4$ (*Trans.*, 1911, xcix, 683), have been prepared. A *dibromodiphenylene* melting at 171° was obtained by the action of bromine on the hydrocarbon, but at the same time a considerable amount of 2:2'-dibromodiphenyl was formed.

Nitration with a mixture of concentrated sulphuric acid and nitric acid (D 1·5) resulted in the formation of a *tetranitrodiphenylene* melting at 223°.

When diphenylene was heated with diluted nitric acid under pressure, there were formed: (1) a *dinitrodiphenylene* melting at 204°, (2) *diphenylene oxide*, (3) *3-nitrophthatic acid*. In preparing the derivatives of diphenylene, a large proportion of the parent substance was invariably converted into waxy and resinous substances.

Attempts to prepare diphenylene by other methods than that originally employed were described. Dry distillation of silver diphenate led to the formation of the lactone of 2-hydroxydiphenyl-2'-carboxylic acid, $\begin{matrix} C_6H_4\cdot CO \\ | \quad | \\ C_6H_4\cdot O \end{matrix}$, but no diphenylene was formed.

Finely-divided sodium reacted rapidly with 2:2'-dibromodiphenyl, forming diphenylene and other substances, of which one agreed in composition with the formula $C_{84}H_{56}Br_2$, and melted at 306°.

328. "*A New Method for the Estimation of Hypochlorites.*" By Herbert Goulding Williams.

Hypochlorites can be titrated with a N/10-solution of hydrazine sulphate, the end point being determined by starch-iodide paper. The action appears to be $N_2H_2 + 2MOCl = N_2 + 2H_2O + 2MCl$.

It is necessary to keep the mixture alkaline throughout, sodium hydrogen carbonate being added if required. Comparison titrations made with N/10 arsenic trioxide and N/10-hydrazine sulphate showed very close agreement.

The author finds that, contrary to the statement of Brown and Shetterly, neither ammonia nor azoimide is formed.

329. "*Ethylation in the Flavone Group.*" By Arthur George Perkin.

Although, except in the case of myricetin, fully ethylated derivatives of flavone colouring matters containing an hydroxyl adjacent to the carbonyl group have not hitherto been prepared by means of ethyl iodide and alkali, no difficulty exists in producing such compounds if an excess of the reagents is employed. Adopting the procedure found serviceable with myricetin (*Trans.*, 1911, xcix., 1725), luteolin (5 grms.) gave *luteolin tetra ethylether*, $C_{15}H_6O_2(OEt)_4$ (Found, Et = 28·67), colourless needles, m. p. 153–155° (4 grms.), whereas from apigenin (5 grms.), *apigenin triethyl ether*, $C_{15}H_7O_2\cdot(OEt)_3$ (Found, (Et = 24·58), prismatic needles, m. p. 189—191° (4 grms.), was prepared. Quercetin from rutin (10 grms.) yielded *quercetin pentaethyl ether*, $C_{15}H_5O_2(OEt)_5$, colourless, prismatic needles, m. p. 116—118° (11 grms.) (Found, Et = 32·86; C = 67·70; H = 6·78), and when hydrolysed with alcoholic potassium hydroxide gave protocatechuic acid diethyl ether, and the hyroxyfisetol triethyl ether, $C_{14}H_{20}O_5$, m. p. 96—97° (Found, C = 62·79; H = 7·39), previously obtained (*loc. cit.*) from myricetin hexaethyl ether. The low melting point of the quercetin pentaethyl ether suggests that this compound may prove to be dimorphous. In a similar way quercetagetin and gossypetin give fully ethylated derivatives, which will be described in a later communication, and there is evidence that other analogous ketonic compounds behave similarly under this treatment.

330. "*The Synthesis of some New Dimethyltetrahydroquinolines.*" By Arthur James Ewins and Harold King.

The synthesis of 4:8-dimethyl-1:2:3:4-tetrahydroquinoline and of the corresponding 4:7- and 4:6-dimethyl bases from the *o*-, *m*-, and *p*-toluidides of acetoacetic acid has been carried out in order to compare their properties with those of a base, α-cytisolidine, a degradation product of the alkaloid cytisine (Freund, *Ber.*, 1904, xxxvii., 16).

The above-mentioned toluidides have not hitherto been isolated. They were prepared by heating mixtures of the toluidine and ethyl acetoacetate, in molecular proportions, to boiling from one to one and a-half minutes. On cooling, the nearly pure toluidides separate out in good yield. On treatment with sulphuric acid at 100° for fifteen minutes they yield carbostyrils, and the latter, by reduction with sodium in alcoholic solution, the dimethyltetrahydroquinolines.

331. "*The Constitution of Cytisine, the Alkaloid of Cytisus Laburnum.* Part I. *The Synthesis of α-Cytisolidine and of β-Cytisolidine.*" By Arthur James Ewins.

By the action of hydriodic acid and phosphorus on cytisine, $C_{11}H_{14}ON_2$, at a temperature of 225—230°, Freund (*Ber.*, 1904, xxxvii., 16) obtained among other products a feebly basic, crystalline solid, cytisoline, $C_{11}H_{11}ON$ (m. p. 198°), and a strongly basic oil, β-cytisolidine, to which he gave the formula $C_{11}H_{15}N$. Cytisoline, on reduction with sodium in alcoholic solution, gave a strongly basic oil of the composition $C_{11}H_{15}N$, which was termed α-cytisolidine on account of its supposed isomerism with β-cytisolidine.

The constitutions of these two bases have now been established by their synthesis. α-Cytisolidine is identical with 6:8-dimethyl-1:2:3:4-tetrahydroquinoline ($C_{11}H_{15}N$), and β-cytisolidine with the corresponding 6:8-dimethylquinoline ($C_{11}H_{11}N$). The formula assigned to β-cytisolidine by Freund is thus inaccurate.

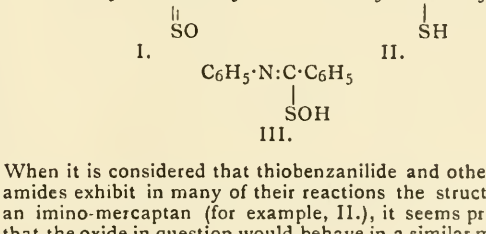
The relationship of the bases obtained by Freund must therefore be as follows:—

Cytisoline, $C_{11}H_{11}ON$ ..	.. (?)-Hydroxy-6:8-dimethylquinoline.
β-Cytisolidine, $C_{11}H_{11}N$	.. 6:8-Dimethylquinoline.
α-Cytisolidine, $C_{11}H_{15}N$	.. 6:8-Dimethyl-1:2:3:4-tetrahydroquinoline.

The constitution of cytisine, from which cytisoline is formed merely by the elimination of the elements of ammonia, remains undetermined.

332. "*Some Reactions of the Sulphoxylic Acids.*" By Percy May and Samuel Smiles.

Barnett and Leete (*Proc.*, 1911, xxvii., 120) have shown that when thiobenzanilide is oxidised with hydrogen dioxide the corresponding thionyl derivative (I.) is formed.



When it is considered that thiobenzanilide and other thioamides exhibit in many of their reactions the structure of an imino-mercaptan (for example, II.), it seems probable that the oxide in question would behave in a similar manner according to the isomeric formula represented by (III.). The suspicion is confirmed by the fact that thiobenzanilide oxide yields a sodium salt, for there can be no doubt that in this substance the metal is attached to the thionyl group. It is therefore evident that under certain conditions thiobenzanilide oxide may be regarded as a sulphoxylic

acid, and at the time when this investigation was planned only one other substance of this class, namely, formaldehyde sulphoxylate, had been isolated. The temporary existence of these substances in certain reactions has been frequently postulated with varying degrees of certainty, and opportunity has now been taken to test the accuracy of certain assumptions concerning their reactivities. Fromm and his collaborators (*Ber.*, 1908, xli., 3397: 1909, xlii., 3816) have advanced the view that in alkaline solution the sulphoxylic acids are unstable, and tend to undergo simultaneous reduction and oxidation, mercaptans and various products of oxidation being formed. This is fully confirmed by the behaviour of thiobenzanilide oxide in alkaline solution. The *sodium* salt may be obtained by rapidly cooling a warm solution of the substance in 10 per cent aqueous sodium hydroxide; it forms very pale yellow needles, which are soluble in cold water, but sparingly so in the cold alkaline medium. The salt is not stable, and if the aqueous solution is warmed it is completely decomposed, yielding benzanilide and thiobenzanlide. It is clear that the latter is formed by reduction of the oxide, and independent experiment shows that the former product is obtained when the oxide is treated with alkaline oxidising agents.

In explaining the reactions of disulphides with concentrated sulphuric acid, it has also been postulated (Prescott and Smiles, *Trans.*, 1911, xcix., 642) that the sulphoxylic acids are capable of condensing in that medium with an aromatic nucleus yielding sulphides, for example: $R{\cdot}SOH + HAr = R{\cdot}S{\cdot}Ar + H_2O$.

Support is given to this assumption by the fact that thiobenzanilide oxide is almost quantitatively transformed by warm sulphuric acid into the phenylbenzothiazole, which has been previously obtained (for example, *Ber.*, 1886, xix., 1068) in other ways:—

$$C_6H_6\begin{cases}\text{—}N\geqslant C{\cdot}C_6H_5\\ HO{\cdot}S\end{cases} = C_6H_4\begin{cases}N\geqslant C{\cdot}C_6H_5\\ S\end{cases} + H_2O.$$

Among other reactions of this oxide mention may be made of that which takes place with dry hydrogen chloride in presence of a dehydrating agent; sulphur is eliminated, and the iminochloride of benzanilide is formed as expressed by the following equation:—

$$\begin{matrix}C_6H_5{\cdot}N{:}C{\cdot}C_6H_5\\ \quad\vert\\ \quad SOH\end{matrix} + HCl = C_6H_5{\cdot}N{:}CCl{\cdot}C_6H_5 + S + H_2O.$$

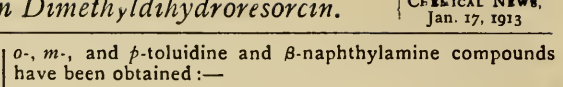
The further investigation has been abandoned owing to the recent discovery (*Ber.*, 1912, xlv., 2965) of other sulphoxylic acids of less intricate structure.

333. "*The Condensation of α-Keto-β-anilino-α-phenylethane and its Homologues with Carbonyl Chloride, Phenylcarbimide, and Phenylthiocarbimide.*" By HAMILTON MCCOMBIE and HAROLD ARCHIBALD SCARBOROUGH.

McCombie and Parkes (*Trans.*, 1912, ci., 1991) have shown that carbonyl chloride and α-keto-β-anilino-αβ diphenylethane can be condensed to give 3:4:5-triphenyl-2:3-dihydro-2-oxazolone. This synthesis has now been extended to α-keto-β-anilino-α-phenylethane, which with carbonyl chloride gives 3:5-diphenyl-2:3-dihydro-2-oxazolone (I.). This reaction has been applied also to compounds in which aniline has been replaced by *o*-, *m*-, and *p*-toluidine and β-naphthylamine.

These oxazolones are stable compounds, and their basicity is so slight that no picrates or hydrochlorides could be isolated.

Brazier and McCombie (*Trans.*, 1912, ci., 2352) acted on α-keto-β-anilino-αβ-diphenylethane with phenylcarbimide, and obtained 1:3:4:5-tetraphenyl 2:3-dihydro-2-glyoxalone. This reaction has now been extended to α-keto-β-anilino-α-phenylethane, which gives with phenylcarbimide, 1:3:4-triphenyl-2:3-dihydro-2-glyoxalone (II.). The reaction occurs in two stages; the two compounds are heated together on a water-bath until a white mass is obtained, which on treatment with alcoholic hydrogen chloride yields the glyoxalone; the corresponding *o*-, *m*-, and *p*-toluidine and β-naphthylamine compounds have been obtained:—



I. II. III.

The glyoxalones yield salts with picric acid, but not with hydrochloric acid. These picrates consist of one molecule of the base combined with one molecule of the acid.

Phenylcarbimide has been replaced by phenylthiocarbimide yielding 1:3:4-triphenyl-2:3 dihydro-2-glyoxalthione (III.).

334. "*Note on the Nitration of p-Hydroxyacetophenone.*" By FRANK GEO. POPE.

Gattermann (*Ber.*, 1892, xxv., 3523) obtained 3-nitro-*p*-hydroxyacetophenone in small yield (11 per cent) by the condensation of *o*-nitroanisole with acetyl chloride in the presence of aluminium chloride. It crystallises in yellow needles melting at 130·5°. The position of the nitro-group was determined by oxidising the methyl ether with dilute nitric acid to 3 nitroanisic acid, which had already been obtained by Salkowski.

Since the hydroxy-ketone is merely a *p*-substituted phenol, there appeared to be no reason why nitration should not be directly attempted, and the following experiment was consequently carried out.

3·5 grms. of the finely-powdered hydroxy-ketone were added in small quantities at a time to a well-cooled mixture of 20 cc. of nitric acid (D 1·42) and 20 cc. of concentrated sulphuric acid, with constant stirring. After half an hour the mixture was poured on to crushed ice, and the faintly yellow precipitate was collected, well washed, and dried. The amount of solid matter so obtained was 3·5 grms., and in the crude state melted at 128—130°. This represents a 75 per cent yield of nitrohydroxyacetophenone.

The nitro compound was then crystallised from boiling water, separating in slender, yellow needles, melting at 135°. (Found, N = 7·92. $C_8H_7O_4N$ requires N = 7·73 per cent.)

Hence the nitro compound is 3-nitro-*p*-hydroxyacetophenone, and further proof is given by the fact that on methylation and subsequent oxidation with dilute nitric acid, 3 nitroanisic acid is obtained. The acid prepared in this manner melts sharply at 190—191°, whereas Salkowski gives 186—187°.

The methyl ether which was also obtained simultaneously by Gattermann is readily prepared by methylating *p*-hydroxyacetophenone in alkaline solution with methyl sulphate, and then nitrating the methyl ether in the manner described above. On oxidation with dilute nitric acid it also yields 3-nitroanisic acid (m. p. 190—191°), a mixed specimen of the acid as obtained by the two different methods also giving the same melting point.

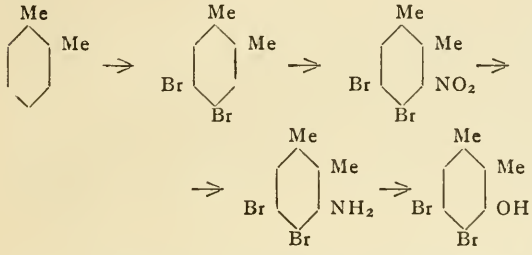
335. "*Bromoxylenols obtained from Dimethyldihydroresorcin.*" (Preliminary Note). By ARTHUR WILLIAM CROSSLEY and SYDNEY SMITH.

In 1903 Crossley and Le Sueur (*Trans.*, 1903, lxxxiii., 110) described experiments on the action of phosphorus haloids on dimethyldihydroresorcin, and showed that both with phosphorus pentachloride and especially phosphorus pentabromide, the resulting substances readily undergo transformation into aromatic derivatives, giving in the latter case bromoxylenols. There were described a mono bromoxylenol melting at 83·5—84° and a dibromoxylenol melting at 96·5°. Both these substances gave on treatment with bromime a tribromoxylenol melting at 183°, which, it was suggested, might be identical with tribromo-*o* 3-xylenol melting at 184°. A second tribromoxylenol was encountered, melting at 177°.

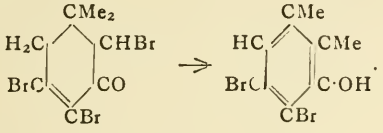
Further work has shown that the reactions are very complicated and susceptible to the slightest variation in experimental conditions. Although by no means com-

plete, it is considered desirable to place on record a brief summary of the definite results so far obtained, as the present authors are unable to continue the work conjointly.

(1) The monobromoxylenol, m. p. 84°, and the dibromoxylenol, m. p. 96·5°, have been proved to be derivatives of *o*-3 xylenol; and although the position of the bromine atom in the former has not yet been decided, the latter has been proved by synthesis to be 4 : 5-*dibromo* o 3-*xylenol*. The synthetic formation is indicated by the following formulæ :—

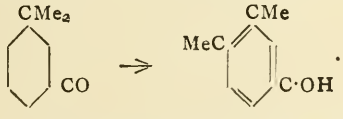


(2) 4 : 5-Dibromo-*o*-3-xylenol has also been obtained by the action of heat or of alcoholic potassium hydroxide on 2 : 4 : 5-tribromo 1 : 1 dimethyl Δ^4-*cyclo*hexen 3-one (tribromoketodimethyltetrahydrobenzene) (*Ibid.*, p. 124), its formation by loss of hydrogen bromide necessitating the wandering of a methyl group from carbon atom 1 to carbon atom 2 :—



(3) There has been isolated from the action of phosphorus pentabromide on dimethyldihydroresorcin a monobromoxylenol melting at 103°. Although the constitution of this substance has not been proved by synthesis, it would appear to be a derivative of *o*-4-xylenol, because on further treatment with bromine it gives a tribromoxylenol, and from this an acetyl derivative, the melting points of which are not lowered on admixture respectively with tribromo *o*-4-xylenol and its acetyl derivative.

In this rearrangement, therefore, a methyl group has again wandered into an ortho-position; but from carbon atom 1 to carbon atom 6, instead of carbon atom 2 :—



The work is being continued, and it is hoped shortly to communicate more detailed accounts of these transformations and of the nature of the resulting products, for which purpose the synthesis of a number of bromoxylenols is being carried out.

336. "*Non-aromatic Diazonium Salts.*" (Preliminary Note). By Gilbert T. Morgan and Joseph Reilly.

The authors have investigated the degree of diazotisability of the following partly aromatic and non-aromatic amines: 4 aminoantipyrine, 6 amino-2 : 4-dimethylpyrimidine, 4 amino 3 : 5-dimethylpyrazole, 4 amino 1 : 3 : 5 trimethylpyrazole, 2 amino 6 oxypurine (guanine), and aminomethyltriazole.

When 4-aminoantipyrine hydrochloride is diazotised with ethyl nitrite in alcoholic solution without excess of mineral acid an uncrystallisable, resinous product is obtained on concentrating the solution. With excess of acid a crystalline diazonium *hydrochloride* is produced, which after prolonged drying in a vacuum over potassium hydroxide corresponds with the formula $2C_{11}H_{11}ON_4Cl,HCl$. The *platinichloride*, $(C_{11}H_{11}ON_4)_2PtCl_6$, the *aurichloride*, $(C_{11}H_{11}ON_4)AuCl_4$, and the very explosive *dichromate*, $(C_{11}H_{11}ON_4)_2Cr_2O_7$, have the normal composition.

Although possessing a chemical constitution closely allied to the aromatic amines, 6-amino-2 : 4-dimethylpyrimidine is not diazotisable under the ordinary experimental conditions, and prolonged treatment with nitrous acid leads to the formation of the corresponding 6-hydroxy-2 : 4-dimethylpyrimidine.

4-*Amino*-3 : 5 *dimethylpyrazole* gives rise to diazonium salts as stable as those of 4-aminoantipyrine, and these substances are being investigated, together with those of 4-amino-1 : 3 : 5-pyrazole.

2-Amino 6 oxypurine does not diazotise under conditions which readily give rise to diazonium salts in the case of aminomethyltriazole.

SOCIETY OF CHEMICAL INDUSTRY.

(London Section.)

Ordinary Meeting, January 6th, 1913.

Dr. W. R. Hodgkinson in the Chair.

The following papers were read and discussed :—

"*Estimation of Glyceryl Acetate in Essential Oils.*" By S. Godfrey Hall and A. J. Harvey.

The authors discuss two methods which have been proposed for the estimation of glyceryl acetate in essential oils. They suggest a process dependent upon the separation and estimation of the glyceryl as such. The glycerol is liberated by a process of saponification and separation of oily matter, and its amount is determined by the triacetin method.

The details of the process and some results obtained with mixtures of known composition are given in the paper.

"*Estimation of Moisture.*" By F. H. Campbell.

The author gives a brief bibliography of the use of calcium carbide as a reagent for the estimation of moisture, and proceeds to describe an apparatus used by him for the gravimetric determination of water by weighing indirectly the acetylene evolved.

He gives comparative results obtained with this and other processes for various substances, such as coal, tea, coffee, butter, &c., and shows that the carbide and vacuum processes give the best agreement.

"*Determination of Moisture in Foods and other Organic Substances.*" By W. P. Skertchly.

In referring to the drying of substances by exposure to sulphuric acid or other dehydrating agent under reduced pressure, the author points out that this method of determining moisture is particularly suitable in the cases of substances which undergo changes when heated, as in the usual method of carrying out the determination, and that, in the case of liquids, it is advisable to pour them upon an absorbent material such as sand, asbestos, &c., to expose the maximum surface.

He gives in tabular form the comparative results of drying such substances as flour, biscuit, maize meal, arrowroot, ground rice, soap, cotton wool, mustard, and manure from hides, to a constant weight *in vacuo* for about twenty-four hours at the ordinary temperature and heating for about two hours (fifteen hours in the case of soap) in a water oven at 100° C.

It is shown that, in all cases, more moisture is yielded when the substances are dried *in vacuo*, and that, in the case of some of the farinaceous materials, the difference amounted to nearly 2 per cent. It was also observed that when the heating at 100° C, was prolonged for more than two hours, the substances began to increase in weight to the extent of a few mm. for each period of one hour.

"*Determination of Water.*" By G. N. HUNTLY and J. H. COSTE.

The authors point to the frequent importance of an accurate determination of water in commercial products, and discuss the following methods for the determination of water in various substances, devoting particular attention to VIII. and IX.

A. *Direct Methods.*

I. Water driven off by ignition, condensed in part of ignition tube, and weighed directly. (Penfold.)

II. Substance heated in a current of dry gas, or in a vacuum, water vapour collected in calcium chloride or sulphuric acid, and weighed.

III. Substance mixed with an excess of a volatile non-miscible liquid such as xylene, distilled, and the water measured under the hydrocarbon layer, with or without corrections for the mutual solubilities of the water and liquid used for its removal.

IV. The material directly heated to 130° C. by a vapour jacket (high pressure steam), the steam given off condensed and measured.

B. *Gasometric Methods.*

V. The substance is mixed with calcium carbide. Acetylene measured.

VI. The substance is mixed with magnesium methyl halide in presence of a suitable dry solvent. Methane measured.

VII. The substance is treated with sodium. Hydrogen measured.

C. *Indirect Methods.*

VIII. Determination of the loss of weight by heating to a definite or indefinite temperature. The usual method.

IX. Prolonged exposure in a vacuum in presence of strong sulphuric acid, either at ordinary or at higher temperature.

They also quote, as being of more or less general application, the conclusions and recommendations embodied in the report of the President and Vice-President of the Committee of the Eighth International Congress on Applied Chemistry on the Determination of Water in Fuel.

NOTICES OF BOOKS.

Whitaker's Peerage, 1913. London: Joseph Whitaker.

THE new feature in the above well-known volume consists in an account of the latest rules issued by the Lord Chamberlain as to the wearing of orders, medals, &c., at public entertainments. This addition is likely to be of value to many of those whose names appear in the book. The "new honours" have increased the number of pages by seventeen over last issue. One addition is recorded in the "Order of Merit," Admiral of the Fleet Sir A. Knyvett Wilson, G.C.B., G.C.V.O., V.C.

The International Whitaker, 1913. London: Joseph Whitaker.

THIS is an entirely new work, and will certainly be welcomed by English-speaking people abroad. The book is divided into four parts. The first deals with the relative functions of the components of the Universe; the second with a description of the land surface of the Earth, physical geography, and ethnographical divisions of Mankind; the third with each Nation, giving its Area, Population, Production, Finances, and other important particulars; the fourth part gives a list of British and American Diplomatic and Consular Representatives in Foreign Countries.

There is a very complete index, occupying close upon forty pages, which includes every reference that can be reasonably demanded.

MISCELLANEOUS.

Royal College of Science, London.—The Fifth Annual Dinner of Old Students of the Royal College of Science, London, will be held at the Cafe Monico, Shaftesbury Avenue, on Saturday, January 25th, 1913, at 7 for 7.30 p.m. The President of the Old Students Association (Sir William Crookes, O.M., D.Sc., F.R.S.) will preside, and the guests will include Sir Alfred Keogh, K.C.B., Sir Henry Miers, F.R.S., Sir Robert Morant, K.C.B., Lt.-Col. Sir David Prain, C.I.E., Sir Amherst Selby-Bigge, K.C.B., Dr. R. T. Glazebrook, F.R.S., and Dr. H. Frank Heath, C.B. With the object of giving the dinner as much as possible the character of a social reunion for old students, the Dinner will be arranged in tables of eight, and tables will be specially arranged for parties as desired. Friends of old students, including ladies, are invited to attend the Dinner. The toast list will be shorter than in previous years, and a programme of music provided. Tickets may be obtained on application to the Secretary of the Old Students Association, 3, Selwood Place, S.W.

MEETINGS FOR THE WEEK.

MONDAY, 20th.—Royal Society of Arts, 8. (Cantor Lecture). "Liquid Fuel," by Prof. Vivian B. Lewes.

TUESDAY, 21st.—Royal Institution, 3. "The Heredity of Sex and some Cognate Problems," by Prof. W. Bateson, F.R.S.

WEDNESDAY, 22nd.—Royal Society of Arts, 8. "Advertising," by Edmund Street and Lionel Jackson.

THURSDAY, 23rd.—Royal Institution, 3. "Birds of the Hill Country," by Seton Gordon, F.Z.S.

—— Royal Society. "Relation of the Islets of Langerhans to the Pancreatic Acini under various conditions of Secretory Activity," by J. Homans. "The Metabolism of Lactating Women," by E. Mellanby. "Colour Adaptation" and "Trichromatic Vision and Anomalous Trichromatism," by F. W. Edridge-Green. "Transmission of Environmental Effects from Parent to Offspring in Simocephalus," by W. E. Agar. "Contributions to the Histo-chemistry of Nerve, on the Nature of Wallerian Degeneration," by H. O. Feiss and W. Cramer. "On Onychaster, a Carboniferous Brittle-star," by I. B. J. Sollas.

—— Chemical, 8.30. "Hydrolysis of Glycol Diacetate," by E. G. Bainbridge. "Constituents of the Rhizome and Roots of *Caulophyllum thalictroides*," by F. B. Power and A. H. Salway. "Ionisation and the Law of Mass Action," by W. R. Bousfield. "Character and Cause of the Blue Fluorescence which Develops in Alkaline Solutions containing Quinol and Sulphite on Exposure to the Air," by T. C. Porter. "Chemistry of the Glutaconic Acids. Part VII. The Normal and Labile Forms of αγ-Dimethylglutaconic Acid and their Reduction to *cis*-αα'-Dimethylglutaric Acid," by J. F. Thorpe and A. S. Wood. "Influence of Water on the Partial Pressure of Hydrogen Chloride above its Alcoholic Solutions," by W. J. Jones, A. Lapworth, and H. M. Lingford. "Quinone-ammonium Derivatives—Part II., Nitro-haloid, Di-haloid, and Azo-compounds," by R. Meldola and W. F. Hollely. "Chemical Nature of some Radio-active Disintegration Products," by A. Fleck. "Action of Ammonia and Alkyl Amines on Reducing Sugars," by J. C. Irvine, R. F. Thomson, and C. S. Garrett. "Mode of Combustion of Carbon," by T. F. E. Rhead and R. V. Wheeler. "Chlorination of Iodophenols. Part II. Action of Chlorine on 2:4:6-Tri-iodo-, 2:6-Dibromo-4-iodo-, 2:4-Di-iodo-, and 2-Bromo-4-iodo-phenol," by G. King and H. McCombie. "Quercetagetin," by A. G. Perkin. "Oxyhydroquinone Phthalein Anhydride and Oxyhydroquinone Benzein," by K. N. Ghosh and E. R. Watson. "2:2'-Ditolyl-5:5'-dicarboxylic Acid," by J. Kenner and E. Witham.

FRIDAY, 24th.—Royal Institution, 9. "Recent Advances in Scientific Steel Metallurgy," by Prof. J. O. Arnold.

—— Physical, 5. "Electrical Conductivity and Fluidity of Strong Solutions," by W. S. Tucker. "Resistance of Electrolytes," by S. W. J. Smith and H. Moss. "Recalescence of Iron Carbide," by S. W. J. Smith and I. Guild.

SATURDAY, 25th.—Royal Institution, 3. "Aspects of Harmony," by H. Walford Davies.

THE CHEMICAL NEWS.

Vol. CVII., No. 2774.

THE PREPARATION OF ANHYDROUS HYDROFLUORIC ACID AND THE ISOLATION OF FLUORINE.

By F. D. CHATTAWAY.

The failure of so many distinguished chemists in their attempts to isolate fluorine induced Frémy, Professor of Chemistry at the École Polytechnique in Paris, to examine with great care the method of preparing hydrofluoric acid, and to study anew its properties, in order to ascertain if possible whether the element could be isolated or not. He recognised the magnitude of his task, for he begins*: —

"In such a work, the difficulties of which are known to all chemists, and coming after such men as Davy, Gay-Lussac, Berzelius, and Thenard, I recognised that I ought not to count upon any such scientific good fortune as would lead me immediately to the discovery of fluorine, but I knew that a general study of the fluorides would be to the advantage of science, since it would complete the history of a series of compounds still little investigated, would probably destroy some accredited errors, and would indicate the path to follow when attempting the isolation of the radical. It is this thought that has constantly sustained me during the prolonged investigation of which I now present the chief results."

Frémy then describes how to prepare pure hydrofluoric acid, it never having been obtained previously absolutely free from other compounds or from water. He states: —

"The acid which is yielded by the action of sulphuric acid on fluor-spar always contains water, sulphuric acid, sulphurous acid, hydrofluosilicic acid, and other impurities. After many fruitless attempts I have given up attempting to purify and dehydrate the crude material obtained thus, and have sought another method of preparing anhydrous hydrofluoric acid."

"The following procedure has given me a very satisfactory result. The substance which I use for preparing the acid is the acid fluoride of potassium. I obtain the salt very easily by pouring a strong solution of hydrofluoric acid into a similar neutral solution of potassium fluoride which has been produced by saturating hydrofluoric acid with carbonate of potash; the acid fluoride which is only slightly soluble crystallises immediately. As thrown down at first it is not pure, but contains hydrofluosilicate of potash, which can, however, be separated by several crystallisations. The acid fluoride of potassium is dried first between folds of unsized paper, next under the receiver of an air-pump, and finally in a drying oven; it can then serve for the preparation of anhydrous hydrofluoric acid. I place the well dried salt in a little platinum retort attached to a platinum receiver, plunged in a freezing mixture. Having connected the neck of the retort to the receiver I carefully heat the salt in the retort strongly so as to drive off the last traces of water, and I only collect the hydrofluoric acid when a part of the salt has been decomposed. . . . The anhydrous hydrofluoric acid obtained by this method is gaseous at the ordinary temperature, but is condensed to a limpid liquid by a mixture of ice and salt. . . . I have also obtained anhydrous hydrofluoric acid by decomposing fluoride of lead by pure and dry hydrogen in a platinum tube. The acid obtained in this way displays all the characteristics of that obtained by calcining the acid fluoride of potassium."

Frémy studied with care a number of metallic fluorides, and showed that although very stable at high temperatures when dry they are rapidly decomposed by steam, hydrofluoric acid being liberated and a metallic oxide left. He found, for example, that on heating mercuric fluoride it volatilised without decomposition when dry, but when damp decomposed giving hydrofluoric acid, mercury, and oxygen. Again, silver fluoride decomposed similarly in presence of moisture, but could not be decomposed by heat when anhydrous. He investigated the action of chlorine and of oxygen on calcium fluoride heated to a high temperature in a platinum tube, and found it to be slight. He further attempted to obtain fluorine from various metallic fluorides, including fluor-spar and potassium fluoride, by electrolysing the fused salts in a platinum crucible, using a platinum rod as a positive electrode. He found that such fused fluorides were decomposed, the metal going to the negative pole, while the platinum rod forming the positive pole was rapidly attacked. A gas was also liberated at the positive pole, which decomposed water, producing hydrofluoric acid, and displaced iodine from iodides. This gas Frémy believed to be fluorine, but he was not able to study it with any care, as from various causes, such as the wearing away of the positive pole or the perforation of the crucible, such electrolysis could only be carried on for a very short time.

Frémy's attempts having proved unsuccessful, in spite of his skill and perseverance, little further was done on the subject until Gore, in 1869, made a fresh systematic study of hydrofluoric acid. Having prepared the pure anhydrous acid by Frémy's method, he determined its boiling-point and vapour pressure at different temperatures, and investigated most of its chief properties in a manner much more exact than had been done previously. Faraday* apparently had discovered that absolutely anhydrous hydrofluoric acid would not conduct an electric current. This observation Gore verified; he showed that when a little water was present the current passed, but only as long as this was being decomposed; when the water disappeared the current stopped.

After a few other unimportant attempts to isolate the element had been made, Moissan, who had been a pupil of Frémy, about the year 1883 took up the subject in a much more careful and systematic manner than had hitherto been possible.

After endeavouring unsuccessfully to obtain the element from one of its compounds with silicon, phosphorus, or arsenic, he came to the conclusion that no reaction carried out at a high temperature was likely to lead to any result, and decided to try again the electrolysis of hydrofluoric acid.

The hydrofluoric acid used was prepared by Frémy's method, and great precautions were taken to obtain it anhydrous. Moissan thus describes its preparation:—

"A known volume of carefully made commercial hydrofluoric acid was taken and one quarter of it neutralised by an alcoholic solution of potassium hydroxide, or better by pure potassium carbonate prepared from the bicarbonate. The two portions were then mixed, and the whole distilled in a lead retort heated in an oil bath to a temperature of 120°. At this temperature silicofluoride of potassium is not decomposed, and an acid was collected free from silica, which commercial hydrofluoric acid always contains in considerable quantity. This distilled acid was then divided into two equal parts, and one was exactly neutralised by pure potassium carbonate. The solution of neutral potas-

* *Annales de Chimie et de Physique*, 1856, [3], xlvii., 5.

* Gore (*Phil. Trans.*, 1869, clix., 189) states that Faraday first made this observation, and refers to the "Handbook of Chemistry" by Leopold Gmelin,' translated by Watts, London, 1858, vol. i., p. 455), where, speaking of hydrofluoric acid, the following statement occurs:—"The hydrated acid is not decomposed only by the water with which it is united suffering decomposition (Faraday)." The only actual statement by Faraday on the subject that I have been able to find is the following which occurs in the "Experimental Researches in Electricity," vol. i., 2nd edition, London, 1849, Section 770, p. 227:— "Solutions of hydrofluoric acid did not appear to be decomposed under the influence of the electric current; it was the water which gave way apparently."

sium fluoride thus obtained was mixed with the second half of the acid, and thus converted into the acid fluoride. The salt itself was obtained by evaporating the solution on a water-bath at 100° in a platinum basin. It was finally completely dried by exposing it in a vacuum over concentrated sulphuric acid. A silver crucible containing two or three sticks of fused caustic potash was also exposed in the vacuous space alongside it. The sulphuric acid and potash were renewed every twenty-four hours for about fifteen days, and the pressure in the bell-jar was maintained at about 20 mm. of mercury. Care must be taken during the drying to powder the salt from time to time in an iron mortar so as to expose fresh surfaces; when completely free from water the acid potassium fluoride falls to powder, and can then be used to prepare the anhydrous acid. It should be noted that properly prepared acid potassium floride is not deliquescent like the neutral salt.

To prepare the acid the dry acid salt was placed as quickly as possible in a platinum retort previously heated to redness so as to free it completely from moisture. The salt was first heated for about an hour to a moderate temperature so that slight decomposition only occurred, the small quantity of acid distilling over during this preliminary heating, which contained any traces of water absorbed during the manipulation of the salt, was allowed to escape. A platinum receiver was next fitted to the retort, which was then more strongly heated, but only to a temperature sufficiently high to decompose the salt slowly; the receiver was cooled by a mixture of ice and salt. From the moment of cooling the receiver all the hydrofluoric acid was condensed. It condenses, as is well known,* to a limpid liquid, boiling at 19·5° C., which is very hygroscopic and fumes strongly in presence of damp air. Hydrofluoric acid thus obtained sometimes contains a small quantity of alkaline fluoride carried over by the acid vapours during the decomposition of the salt. It is not necessary for the end in view to avoid this as it helps to render the acid a conductor. If it is desired to obtain pure hydrofluoric acid a much larger platinum retort must be used, and the acid vapours must be led to the condenser through a long platinum tube sloping upwards from the retort, and kept above the temperature at which the acid boils."

Hydrofluoric acid is so hygroscopic that it can be kept in the anhydrous state only with the greatest difficulty, and it was found that the one practicable procedure was to prepare it immediately before use.

With acid prepared thus, Moissan confirmed Gore's observation that anhydrous hydrofluoric acid does not conduct. He states that if the acid contains a small quantity of water, either added intentionally or present through the acid having been prepared carelessly, this alone is decomposed, ozone being set free at the positive pole. As the water is broken up the conductivity of the acid diminishes, and when the whole disappears and the acid becomes anhydrous the current no longer passes. Moissan states:—"In several experiments an acid so free from water was obtained that a current of 35 ampères furnished by fifty Bunsen cells was totally stopped."

Guided by the experience gained in his previous attempts to electrolyse arsenic fluoride, Moissan then tried the effect of adding to the non-conducting hydrofluoric acid a small quantity of very dry potassium hydrogen fluoride, KF.HF. This was found to dissolve readily in the anhydrous acid. Moissan states:—"If fragments of potassium hydrogen fluoride are added to anhydrous hydrofluoric acid contained in a platinum crucible they are seen to disappear rapidly, potassium hydrogen fluoride being very soluble in the anhydrous acid."

Submitting such a solution to electrolysis, he found that the current passed and that a gaseous product was liberated at each electrode. To enable the products to be collected separately the well known platinum U-tube apparatus was devised.

* Compare Gore (*loc. cit.*).

The electrolysis was carried out at a very low temperature, to prevent any gaseous product formed being largely diluted with the vapour of hydrofluoric acid and to diminish the risk of the apparatus being attacked destructively by any fluorine liberated. For this purpose the U-tube was immersed in a bath of methyl chloride, the temperature of which, although it boils under the ordinary pressure at - 23°, can easily be lowered to - 50°, when its evaporation is increased by aspirating through it a current of dry air.

Moissan subsequently found that a product more free from hydrogen fluoride could be obtained by conducting the electrolysis at a temperature lower than this, and in his later experiments used a bath of acetone holding solid carbon dioxide in suspension, with which a temperature of − 80° could be obtained.

Moissan thus describes an experiment:—"While the hydrofluoric acid was being prepared the platinum U-tube and the electrodes were dried in an air bath at 120°. About 6 to 7 grms. of thoroughly dried acid potassium fluoride were introduced into the apparatus, the stoppers were very carefully screwed in and covered outside with a coating of melted shellac. The U-tube was then fixed into a glass cylinder by a cork, the entrance of moisture being prevented by attaching to the outside tubes drying tubes containing recently fused potash. Methyl chloride was then introduced into the glass cylinder, and the temperature* in this way reduced to 23°. . . . The hydrofluoric acid was then drawn into the apparatus, from the receiver in which it had been condensed, through one of the side tubes by means of a mercury aspirator. In each experiment from 15 to 16 grms. of acid were used. . . . As soon as the current was passed gas was regularly evolved from each pole. At the negative pole hydrogen was obtained which burnt with an almost invisible flame, yielding water vapour, the properties of which could easily be verified. At the positive pole a gas was disengaged, apparently colourless and endowed with very great chemical activity. . . ."

Fluorine was thus isolated for the first time by Moissan on June 26th, 1886. The apparatus used at first was made wholly of platinum, but it was subsequently found that a copper U-tube could be employed.

In early experiments the electrodes were made of platinum containing 10 per cent of iridium, this alloy being somewhat less readily attacked than pure platinum; later electrodes of pure platinum were used, made club shaped at the end so that they would resist the attack of the fluorine for a longer time.

The positive electrode was often completely corroded away during an experiment, but the U-tube was never found to have lost any weighable amount of platinum.

In order to study the properties of fluorine it was absolutely necessary to obtain it free from the vapours of hydrofluoric acid derived from the acid undergoing electrolysis. To do this the fluorine was passed through a little platinum worm serving as a condenser, and cooled by a bath of methyl chloride to about - 50°.

The gas issuing from this only carries away the small quantity of hydrogen fluoride corresponding to its vapour pressure at this temperature, which is about 70° below its boiling-point. It was freed from the last remaining traces of hydrofluoric acid by passing it through two small platinum tubes filled with fragments of fused sodium fluoride, which does not attract moisture as does potassium fluoride, and which combines readily at the ordinary temperature with hydrogen fluoride. Using 26 to 28 Bunsen cells mounted in series, and employing an apparatus containing from 90 to 100 grms. of anhydrous hydrofluoric acid in which 20 to 25 grms. of potassium hydrogen fluoride had been dissolved, Moissan obtained a yield of 2 to 3 litres of fluorine per hour.

* Moissan again notes that a higher temperature than this, say - 10°, is insufficient to prevent the gas escaping at each pole from being mixed with a large excess of the vapour of hydrogen fluoride.

Since pure anhydrous hydrofluoric acid does not conduct the current, which only passes when it contains acid potassium fluoride, Moissan considers that this salt undergoes electrolysis, fluorine and potassium being produced. The fluorine escapes at the positive pole, while the metal set free at the negative pole immediately reacts with the hydrofluoric acid present, liberating hydrogen and reforming acid potassium fluoride.

At a sufficiently low temperature fluorine can be both liquefied and solidified. When cooled by liquid air* boiling in a vacuum it condenses to a clear yellow liquid of density 1·14, which under ordinary atmospheric pressure boils at about −187°. When cooled† in liquid hydrogen it solidifies to a pale yellow solid, which melts at about −223°, and on cooling still further becomes perfectly white at about −252°.

The density of fluorine was determined by Moissan by weighing about 100 cc. of it in a small light platinum flask. In his first experiments he obtained a density considerably lower than that required by the formula F_2. It was suggested by Brauner‡ that this low density might be due to the molecules being partially dissociated even at the ordinary temperature, and that the intense chemical activity of the substance might be due to the atomic condition of the gas. Moissan, however, afterwards showed that the low number he originally obtained was due to the fluorine not having been completely freed from the vapour of hydrofluoric acid, and that if pure its density agreed perfectly with that required by the diatomic formula F_2.

Fluorine combines explosively with hydrogen at the ordinary temperature even when light is excluded, as is seen from the explosions which took place in the generating tube if, owing to a difference of pressure or to the hydrogen fluoride being used up, the two gases came into contact. Liquid fluorine cooled to −210° by liquid air boiling under a low pressure combines immediately with hydrogen, producing a flame and considerable development of heat. Explosive combination§ accompanied by incandescence also results when solidified fluorine is brought into contact with liquefied hydrogen at −252°, showing that at a temperature only about 20° above the absolute zero not only will combination take place, but that these elements still possess strong chemical affinity.

THE SOLUBILITY OF BASIC SLAG.

By JOHN HUGHES, F.I.C.

In a paper on "Basic Superphosphate," read by the writer in April, 1901, before the London Section of the Society of Chemical Industry, it was pointed out that the statement that ordinary basic slag contained 20 per cent of free caustic lime was obviously incorrect, because such an excess of lime would indicate a wasteful method of manufacture, for lime was only added in sufficient quantity to remove the phosphorus and silica existing in the original iron ore.

It was further mentioned that probably 2 or 3 per cent was the utmost caustic lime usually present in commercial basic slag. Recent investigation by the writer tends to indicate that the existence of caustic lime, even in small proportion, exerts a most important influence in rendering the slag soluble in the 2 per cent solution of citric acid, which, under the provisions of the Fertilisers and Feeding Stuffs Act, 1906, has been prescribed as the standard solvent for this material.

In the following analyses the figures represent the general composition, also the relative solubility in the above solvent :—

General Composition.

	No. 1.	No. 2.	No. 3.	No. 4.
Fine powder passed through standard sieve, 10,000 holes to square inch	90·89	75·74	70·92	96·15
Total lime	51·85	48·10	46·45	41·97
Phosphoric acid	19·45	17·90	18·80	10·95
Oxides of iron, manganese, magnesia, &c.	23·75	27·20	27·45	30·07
Insoluble silicious matters ..	4·95	7·80	7·30	17·01
	100·00	100·00	100·00	100·00
Equal to phosphate of lime	42·46	39·08	41·04	23·91
Containing caustic lime ..	3·66	2·50	1·43	0·22

Solubility in 2 per cent Citric Acid Solution after Agitation in Bottle for Half-an-hour.

Soluble lime	42·77	40·76	37·52	26·12
Soluble phosphoric acid ..	15·60	16·55	16·30	1·80
Equal to phosphate of lime	34·05	36·13	35·58	3·93

It will be noticed that fine grinding *alone* does not ensure future solubility, for Sample 4, which is the finest ground, shows the *lowest* solubility; while Sample 3, which is the coarsest powder, shows a very high solubility.

It is interesting to notice that the citric solution, though it fails to dissolve much of the phosphoric acid in No. 4, dissolves a very considerable proportion of lime, namely, 26·12 per cent, whioh probably explains why basic slags which yield a low solubility of phosphoric acid, nevertheless, supply a relatively large quantity of lime in a very finely divided state, and consequently if applied to soils deficient in lime and decidedly damp and sour, may produce a very satisfactory improvement in the pasture at a relatively *small cost*.

It might be contended that the solubility might be due to the relatively high proportion of lime associated with a low proportion of silica; but such is not the case, for a sample containing 18·20 per cent of silica and only 39·99 per cent of lime showed a solubility of 35·36 phosphate of lime, though the grinding was only 77·12.

It seems, indeed, quite natural that the presence of caustic lime causes the minute fragments of the slag to burst on the absorption of moisture, and thus mechanically materially promotes the subsequent solvent action of the citric solution, and that when caustic lime is not present the solvent action is very much less effective.

79, Mark Lane, London, E.C.

* *Proc. Chem. Soc.*, 1897. xiii., 171.
† *Comptes Rendus*, 1903, cxxxvi., 641.
‡ *Zeit. Anorg. Chem.*, 1894, vii., 1.
§ *Comptes Rendus*, 1903, cxxxvi., 643.

RARE EARTH REACTIONS IN NON-AQUEOUS SOLVENTS.*

By O. L. BARNEBEY.

(Concluded from p. 31).

4. Fractionation of Yttrium Earths by Precipitation with Tartaric Acid from Acetone Solutions.

When tartaric acid is added to an acetone solution of the earth nitrates in sufficient quantity to unite with only a small portion of the earths present, a semi-flocculent white precipitate forms. If this precipitate is filtered from the mother-liquor and tartaric acid added again, the second precipitate is formed much more slowly and is more crystalline than the first. After two or three fractions have been removed it is noticed that considerable tartaric acid must be added in excess to start precipitation. Soon it is observed that the precipitate formed by the introduction of a considerable quantity of reagent will re-dissolve when the solution is agitated and then slowly crystallises out on the sides and bottom of the containing vessel. Gentle disturbance will cause the crystalline tartrate layer

* *Journal of the American Chemical Society*, xxxiv., No. 9.

to settle to the bottom in large leaflets, and the clear solution can be decanted readily from the precipitate. The last several fractions do not form until a number of hours have elapsed. The last fraction is best precipitated by means of oxalic acid.

Preparation of Solutions.

1. A saturated solution of tartaric acid in acetone. Tartaric acid is only moderately soluble in acetone, consequently solution is effected by adding an excess of acid to acetone and allowing the solution to stand for some time with occasional shaking.

2. A dilute acetone solution of the earth nitrates. The oxides are dissolved in nitric acid and evaporated over a steam-bath until the nitrates crystallise and are free from water. The resulting nitrates are extracted with acetone. If solution is not effected readily the residue should be transferred to a flask and allowed to remain in contact with the acetone for some time with occasional agitation. Should solution still be incomplete the residue is filtered out, again dissolved in nitric acid, evaporated, and extracted again. Usually more or less of the basic salts are formed which seem to be insoluble in acetone, hence reconversion to normal nitrate is necessary before complete solution results. This acetone solution of the nitrates is then diluted with a convenient amount of acetone.

Completeness of Precipitation.—About 0·5 grm. of mixed yttrium group oxides was dissolved in nitric acid, evaporated to dryness, dissolved in acetone as outlined above, diluted to 100 cc. with acetone, and tartaric acid in acetone added slowly with constant stirring until precipitation was apparently complete. The precipitate was removed by filtration, and more tartaric acid added to the filtrate. A precipitate slowly formed. It was allowed to stand about twelve hours, again filtered, and the filtrate tested for the presence of earths by the addition of ammonium oxalate and ammonia. A slight precipitate formed.

Occlusion occurs to some extent when the precipitant is added rapidly to the earth nitrate solutions for the first fractions. Consequently, until that stage of the fractionation is reached when the addition of the fractional amount of reagent produces no immediate precipitation, the addition of tartaric acid should be made slowly with constant agitation of the earth solution The more dilute the solution the less is the occlusion effect.

In moderately dilute solutions then we have an almost ideal precipitate to handle—crystalline, easily filtered, and slow forming, thus allowing a maximum opportunity for equilibrium to be established preceding the removal of each fraction.

Fractional Separations.

About 30 grms. of yttrium group oxides from fergusonite were converted to nitrates, dissolved in acetone, and diluted with acetone to about 400 cc. A solution of tartaric acid in acetone was added drop by drop from a burette with constant stirring until the solution became turbid, due to the forming tartrate, then 10 cc. were added in excess. After thorough shaking and subsiding of the precipitate the solution was filtered. The residue was ignited to oxide and called fraction one. To the filtrate tartaric acid was added, 5 cc. in excess of the amount used for the first fraction, and the fractionation continued. Seven fractions were obtained in all. The filtrate from the seventh precipitation was treated with ammonium oxalate and ammonia, and the resulting precipitate ignited to oxide, which constituted fraction 8.

No. of fraction.	Colour.	Grms.	Equivalent weight.
1.	Almost white, chamois tinge	2·5	155·8
2.	Almost white, chamois tinge	4·0	140·7
3.	Somewhat darker	4·5	139·1
4.	Dark chamois	4·5	133·9
5.	Dark chamois	5·5	134·0
6.	Dark chamois	4·5	135·8
7.	Dark chamois (lighter) ..	3·5	123·8
	Almost white	1·0	112·3

Spectroscopic examination of 10 per cent solutions showed a concentration of didymium, dysprosium, holmium, and erbium in fractions 5, 6, and 7. Erbium seemed also to concentrate slightly in fraction 2. The equivalent weights show a concentration of ytterbium in the first, and yttrium in the last fractions.

Fractions 2 and 3 were combined and refractionated, giving the following fractions:—

No.	Colour of oxide.	Equiv. weight.
1.	Very light buff (almost white) .	144·3
2.	Very light buff (darker)	—
3.	Very light buff (darker)	—
4.	Almost white	—
5.	Chamois	126 2
6.	Light chamois	—
7.	Light chamois	—
8.	Light chamois	—
9.	Lighter chamois	—
10.	Light buff (pink tinge)	117·0
11.	Much lighter buff	—
12.	Very light buff (almost white) .	110·5

Fractions 4, 5, 6, and 7 were combined and refractionated, resulting as follows:—

No.	Colour of oxide.	Equiv. weight.
1.	Very light buff (almost white) .	131·5
2.	Much darker buff	134·2
3.	Much lighter buff	138·8
4.	Much lighter buff	130·0
5.	Deep chamois	131·4
6.	Much lighter chamois	126·8
7.	Still lighter chamois..	123·9
8.	Light buff (pink tinge)	120·5
9.	Very light buff	118·2
10.	Very light buff (almost white) .	113·6

The last five were small fractions. A slight accumulation of erbium was noted spectroscopically in fractions 2 and 3 of both series, but the main portion appeared to be concentrating in fractions 9, 10, and 11 of the first series, and 7, 8, and 9 of the second.

Seven fractions which had been previously extracted from monazite were next fractionated, yielding fractions of the same general order as those above. Below are listed the first and last fractions.

		Equiv. weight.
Series I.:—		
First fraction	Yellow to buff oxide	133·0
Seventh fraction	Almost white oxide..	—
Series II.:—		
First fraction	Deep buff oxide ..	128·8
Sixth fraction	Light yellow oxide..	114·5
Series III.:—		
First fraction	Light yellow oxide..	121·3
Seventh fraction	Light yellow oxide..	115·9
Series IV.:—		
First fraction	Light yellow oxide..	118·6
Sixth fraction	Very light buff oxide	110·7
Series V.:—		
First Fraction	Almost white oxide	115·9
Sixth fraction	Almost white oxide	110·5
Series VI.:—		
First fraction	Almost white oxide	120·9
Fifth fraction	Almost white oxide	110·8
Series VII.:—		
First fraction	White oxide	117·2
Sixth fraction	White oxide	113·1

Spectroscopic examination of these series showed that, of the earths giving absorption bands, holmium was the first to concentrate, followed by erbium and dysprosium, the last

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wo being less separated than any of the others. Erbium seems to concentrate toward the first and also in the last fractions with the first few fractionations. However, this seeming double behaviour is in this case only temporary, as further fractionation removes the erbium from the early portion of the series and places it toward the end of the series with the remainder of the erbium. In a recent investigation of the action of picric acid as an agent for the fractionation of the earths from aqueous solutions, Dennis and Bennet (*Journ. Am. Chem. Soc.*, xxxiv., 7) observe that erbium tends to concentrate in two places in the series. This behaviour is also characteristic of the tartaric acid fractionation in acetone. The atomic weight determinations indicated the accumulation of yttrium in the last fractions.

Some earths containing a little didymium originally from monazite were fractionated yielding 34 fractions, which were united with the previous fractions according to (1) the relative order of precipitation, (2) colour of oxides, (3) spectroscopic absorption lines. They were then refractionated. One hundred and seventy-one fractions were obtained. Again the fractions were united and refractionated and 164 fractions resulted, each series of which was subjected to spectroscopic examinations and to the determination of equivalent weights. The following end fractions are given, inasmuch as they are representative of the entire set of series: —

		Equiv. weight.
Series I. :—		
First fraction	Almost white oxide ..	170·8
Fourth fraction	Almost white oxide ..	129·4
Series II. :—		
First fraction	Almost white oxide ..	168·4
Tenth fraction	Dark chamois oxide ..	126·3
Series IV. :—		
First fraction	Verv light buff oxide ..	134·1
Twelfth fraction	Very light chamois oxide	110·5
Series IX. :—		
First fraction	Buff, with slightly pink tinge	125·1
Thirteenth fraction	Chamois oxide	114·1
Series XIII. :—		
First fraction	Almost white oxide ..	120·2
Twelfth fraction	Almost white oxide ..	105·8
Series XIV. :—		
First fraction	Almost white oxide ..	115·8
Ninth fraction	Almost white oxide ..	107·1
Series XVI. :—		
First fraction	Almost white oxide ..	107·6
Seventh fraction	White oxide	93·2

Spectroscopically those earths giving absorption bands correspond to the order – holmium, erbium, and dysprosium. From the equivalent weight determinations the conclusion can be drawn that ytterbium (lutec um and neoytterbium) is the first member of the group precipitated, and yttrium last. Hence the serial order is ytterbium, holmium, erbium, and dysprosium, yttrium.

Composition of the Precipitrated Tartrates.—The precipitrated tartrates carry down tartaric acid, which is difficult to wash out with acetone. After thorough washing and drying by suction the tartrates contain only traces of acetone, in fact a negligible quantity. Ignition gives an oxide content which shows the precipitate to be acid. However, if the tartrates are dissolved in a measured volume of standard acid and the excess of free acid titrated with standard alkali, using phenolphthalein as indicator, the tartrates give acidity in excess of the amount calculated as being possible from the percentage of oxide obtained. This deportment indicates that the earth tartrates become basic during titration, liberating free acid, which is subsequently titrated.

Summary.

In this investigation a contribution to the systematic non-aqueous chemistry of the rare earths is given. A number of the reactions of the common acids and bases with the yttrium group, neodymium, lanthanum, and cerium have been studied, utilising acetone as solvent. In specific cases other solvents have been used. The reactions are of the same general order as those in aqueous solution, except that the solubilities vary greatly, hence the results of interaction of reagent with earth are vitally different in many cases. In general it may be said that the earths form more compounds insoluble in acetone than in aqueous solution. In many instances compounds have been found to be insoluble in acetone and soluble in water, hence the use of a solvent like acetone furnishes a means of preparation which can not be attained with water as the reaction medium. Especially is this the case with certain compounds of the acids and the alkaloids. A new field of rare earth study is introduced by the preliminary work done with the alkaloids.

The basic nitrate scheme of fractionation, using acetone as solvent, gives a rapid method for the separation of cerium from the mixed earths as well as fractionating the others at the same time.

A separation of the yttrium group, using tartaric acid as the precipitant, has been found to be very effective for fractional purposes. The serial order established is ytterbium (lutecium and neoytterbium), holmium, erbium and dysprosium, and yttrium.

This investigation was undertaken at the suggestion of Prof. Lenher, who has kindly co-operated throughout the work. Gratitude is also expressed to Prof. Fischer for suggestions, especially during the alkaloidal study. To Mr. H. S. Miner, of the Welsbach Company, we are grateful for most of the material used.

MONEL METAL.*

By RICHARD H. GAINES.

(Concluded from p. 305).

Properties.

In appearance Monel metal resembles nickel in colour. It takes a brilliant polish, nearly equal to that of silver, which it retains indefinitely. On long exposure the surface assumes a greyish cast, which may be removed with a polishing cloth. It is somewhat tougher than mild steel, but, nevertheless, it machines very easily. A lathe can be run at about the same speed on Monel metal as on mild steel, and the metal can be soldered, brazed, electrically welded, and successfully drawn.

Some of the Physical Constants of Monel Metal.

(Physical data in part from John F. Thompson, *Eng. and Min. Journ.*, 1911, xci.).

Melting-point	1360° C. or 2480° F.
Specific gravity (cast)	8·87
Weight per cu. in. (cast)	0·319 lb.
Weight per cu. in. (rolled)	0·323 lb.
Coefficient of expansion, 20 to 100° C.	0·00001375 per 1° C.
Electrical resistivity temperature coefficient 0·0011 per 1° F. = 256 ohms per mil-foot.	
Electrical conductivity (copper 100 per cent)	4 per cent
Heat conductivity	One-fifth of that of copper
Shrinkage	¼ inch per foot
Hardness, cast material (Shore scleroscope	20 to 23
Hardness, hot rolled rods (average (Shore scleroscope)	27

* From the *Journal of Industrial and Engineering Chemistry*, iv., No. 5.

A comparison of some of the properties of copper, nickel, and Monel metal, as reported by recent authority (*Transactions of the American Institute of Mining Engineers*, 1910, xli., 310), is given below :—

	Copper rolled.	Nickel rolled.	Monel metal. Cast.	Rolled.	Annealed.
Tensile strength, lbs. per sq. in.	34,000	75·500	85,000	100,000	110,000
Elastic limit, lbs. per sq. in. ..	18,000	21,000	40,000	50,000	80,000
Elongation in 2 in. per cent	52	43 9	25	30	25
Contraction, per cent	57	57	25	50	50
Melting-point ..	1084° C.	1500° C.	1360° C.		

Recent tests (*Ibid.*, 1911) of Monel metal at laboratory of William Sellers, Philadelphia, Pa., are :—

	Hot rolled rods.	Sand castings.
Elastic limit, lbs. per sq. in. ..	58,873	37,427
Breaking strength, lbs. per sq. in.	86,899	78,236
Elongation in 2 inches, per cent..	40·0	38·5
Reduction of area, per cent.. ..	60·5	34·0
Modulus of elasticity	22,000,000 to 23,000,000	

In all the technical reports relating to Monel metal, it is referred to as a non corrosive alloy. Redfield (*American Machinist*, xxxiv., I., 513—514) and other writers claim that the castings have the strength and many other properties of cast steel, while they have greater resistance to corrosion from sea-water, superheated steam, and corrosive chemical solutions than the bronzes. Owing to its remarkable stability in sea-water, the U.S. government is now equipping its battleships with propellers of this material, these being cast in single pieces. Propellers have already been made for the North Dakota and for battleships of other countries, some of the latter being 15 ft. 6 in. in diameter in a single piece, weighing 16.000 lbs. After eighteen months' service, it is said that the wear and corrosion of these propellers was found to be practically negligible. It was further found that they resist bending to such an extent that they are not so subject to loss of efficiency as propellers which yield under heavy backward pressure against the water.

Experiments made at the laboratory indicate that Monel metal possesses about the same resistance to corrosive action as the better known bronzes. Specimens of several bronzes, Monel metal, and steel were weighed and embedded in rich earth, which was kept wet for six months by periodical additions of very dilute solutions of corrosive salts. At the end of the test period all the specimens were taken out, scrubbed, dried, and weighed to ascertain the comparative loss from corrosion. The results were as follows :—

	Per cent loss.
Phosphor bronze	0·09
Tobin bronze	0·11
Monel metal	0·12
Parsons manganese brass.. ..	0·12
Muntz metal	0·33
Steel	1·04

Another test of the same kind, under somewhat different conditions, but the same period, gave about the same relative results.

One advantage in favour of Monel metal in these tests was that it presented the least change in appearance as a result of the corrosive action.

Casting.

While no trouble has been experienced in rolling Monel metal, considerable difficulty has been met with in some foundries in getting sound castings. Incidentally, it may be remarked that nickel-copper alloys have a great tendency to develop blow-holes on casting, due to occluded gases. This is another indication of the absence of a chemical compound, since the presence of a compound in an alloy seems to have the influence of preventing blow-holes, and closing the grain. Monel metal requires special precautions in casting on account of dissolved oxides and gases, which, if not removed, would render the ingots unsound. Successful castings have been made in small foundries by adding 2 ounces of magnesium per 100 lbs. of the alloy, before pouring.

Unsound castings may also arise from gases that are liberated in the cores of the patterns, and from the fact that the freezing-point of the metal is so many hundred degrees above that of brass or bronze that these gases cannot escape before they are trapped by the freezing metal. This necessitates the use of the same methods as for fine steel castings. It must be remembered that the actual temperature of Monel metal cannot be much lower than 1550° C. The art of casting Monel metal is closely related to the art of casting steel, as distinct from the art of casting brass, bronze, or cast iron. It really involves the art of handling the finest steel castings. The practice of casting Monel metal is, therefore, very similar to that followed in steel foundries. The melting equipment of the plant consists of standard reverberatory furnaces, which are fired with oil, the fuel being fed by gravity. The metal is charged into the furnace in the form of pigs or slabs which are about $15 \times 8 \times 3$ inches in dimensions, and weigh about 85 lbs. The melting-point is about 2500° F., and eight hours are required to the heat. No fluxes nor alloys are necessary. Because of the relatively scant knowledge of nickel and its peculiarities, the handling of Monel metal requires expert attention in the melting.

The industry of making Monel metal castings is now past the experimental stage, and is being successfully accomplished in at least three foundries in New York and New Jersey. Mr. Leonard Waldo, consulting engineer, is authority for the statement that notable success has been achieved at the Johnson Foundry of Spuyten Duyvil in the casting of this metal. The Bayonne Casting Company, of Bayonne, N.J., and the Riverside Steel Company, of Newark, N.J., are other foundries that are making good castings.

Uses.

Although a comparatively new alloy, because of the resistance to corrosion, its strength, and the readiness with which it may be machined, Monel metal has already found many important uses. These include pump cylinders for handling salt water, propeller wheels, rudders, centre boards, deck fittings, mining screens, water ends of pumps, linings, valves, shafts, piston rods, and plumbing fixtures subject to corrosive influences.

In the rolled metal there is a wide range of usage. Striking instances in the past include the roofs of the new terminals of the Pennsylvania Railroad in New York, and the Chicago and North-western Railroad in Chicago, which were covered with Monel metal. The sheets have also been used on several large office buildings in New York, and on industrial plants subject to severe corrosive conditions where copper had proved unsatisfactory.

Rigid physical specifications should be the rule wherever Monel metal is considered for use in any form of engineering construction. With reference to chemical specifications, it would be impracticable to set any narrow limits as to chemical constituents, owing to the somewhat variable character of the ore and the method of manufacture. It is not believed, moreover, that such limits are necessary in order to insure the desired physical properties of strength and durability. If too close limits are set on chemical constituents the metal so specified might be obtained, but at a cost that would render its use prohibitory. —*Journal of Industrial and Engineering Chemistry*, iv., No. 5.

THE BEHAVIOUR OF NITROGLYCERIN WHEN HEATED.*

By WALTER O. SNELLING and C. G. STORM.

Introduction.

The Bureau of Mines, under the authority of the Act that established it, is conducting investigations relating to the use of explosives. These investigations include physical and chemical tests, which are carried on chiefly at the experiment station of the bureau at Pittsburgh, Pa. A study of the behaviour of nitroglycerin when exposed to heat has been made in the explosives laboratory at that station and is described in this paper.

A knowledge of the action of heat upon nitroglycerin is very important, because of the information thereby gained in regard to the stability of explosives and the behaviour of large masses of explosives when burning, and the relation of such facts to fires in magazines and nitroglycerin factories.

Very little information on the behaviour of nitroglycerin at high temperatures is available in the literature relating to explosives. The importance of such information has been fully recognised by investigators, and a number of attempts have been made to obtain it by experimental study. Results of even approximate accuracy have been difficult to get, because of the readiness with which nitroglycerin explodes when its temperature is slightly raised and because of the destructive effects of the explosion of even very small quantities of the substance.

Previous Investigations.

Several investigators, notably Champion (*Zeit. Chemie*, 1871, p. 351), de Bruyn (*Recueil des Travaux Chimiques des Pays-Bas*, 1895, xiv., 131), Hagen (referred to in Escales, "Die Explosivstoffe, iii., 160), and Munroe (*Jour. Am. Chem. Soc.*, 1890, xii., 57), have devised most ingenious methods for indirectly observing the effect of heat upon nitroglycerin, and the knowledge available at the present time in relation to this subject is derived almost entirely from the studies that have been made, at considerable personal hazard, by the investigators named.

The effect of temperatures below 100° C. upon nitroglycerin has been the subject of many researches, and these have given important information to manufacturers and users of explosives. The common tests (known as heat tests) for determining the stability of nitroglycerin and nitroglycerin explosives depend either upon the time required for the production from nitroglycerin (at temperatures below 100° C.) of oxides of nitrogen sufficient to colour potassium-iodide-starch or other test paper, or upon the measurement in some other manner of the oxides of nitrogen evolved.

One of the early studies to determine the effect of temperatures above 100° C. upon nitroglycerin was made by Leygue and Champion (*Comptes Rendus*, 1871, lxxiii., 42, 1478) and by Champion (*Zeit. Chemie*, 1871, p. 351). The work was based upon the known distribution of temperature in a metal bar, heated at one extremity. A copper bar was used provided with cavities at equal intervals. These cavities were filled with oil or an alloy of low fusing point, and by means of thermometers placed within them the interior temperature of the bar was measured. A curve was prepared showing the temperature at all points along the bar. When equilibrium was reached, as indicated by the reading of the thermometer, small quantities of the explosives to be tested were placed at different points along the bar until the desired effects were obtained. A screen was interposed between the source of heat and the samples being tested to keep them from being affected by radiant heat. Tested in this way, nitroglycerin was found to detonate at the temperature of 256° C., and ebullition took place at the temperature of 185° C.

It is evident that the method just outlined has many serious faults, and must necessarily fail to give results that are at all accurate. Lobry de Bruyn (*Recueil des Travaux Chimiques des Pays-Bas*, 1895, xiv., 131; *Jahresbericht über die Fortschritt der Chemie*, 1895, lxviii., 1000) noted that it was very doubtful if the explosive could really reach the temperature of the bar, and he therefore concluded that the temperatures obtained by Leygue and Champion were really far higher than they should have been. For example, Champion had ascertained that nitrocellulose (guncotton) could be heated to 220° C. before ignition occurred, while Lobry de Bruyn failed, as most others have since done, to bring nitrocotton to a temperature higher than than 190° C. without causing explosion. Lobry de Bruyn heated nitroglycerin, in quantities up to 2 cc., in a flask immersed in a glycerin bath containing a thermometer, but in his experiments he kept the nitroglycerin under reduced pressure by means of an air-pump connected to a side-necked tube of the flask, and accordingly he did not obtain results of direct value in determining the action of heat upon nitroglycerin under ordinary conditions.

Charles E. Munroe found the firing temperature of nitroglycerin to be 203° to 205° C. (*Jour. Am. Chem. Soc.*, 1890, xii., 57). In his experiments, the sample of explosive (one drop in the case of nitroglycerin) was placed at the bottom of a thin copper cartridge case, ⅝ inch in diameter and 1⅛ inches long. The copper case was then immersed in a bath of paraffin or molten tin contained in an iron vessel. The initial temperature of the bath was noted by means of a thermometer suspended at the side of the cartridge case to a depth of 1 inch (the cartridge case when put in the bath being plunged so that its lower end was also immersed to a depth of about 1 inch). The temperature of the bath was then quickly raised and the reading of the thermometer at the moment the nitroglycerin exploded was noted as the firing point. Munroe's results were as follows:—

Determinations by Munroe of Firing Point of Nitroglycerin.

Initial temperature.	Firing point.
150° C	204° C
180	203
185	204
190	205
190	205
195	205

Nobel (*Dingler's Polyt. Journ.*, 1867, clxxxiii., 221) gives 180° C. as the firing point of nitroglycerin. Abel (*Dingler's Polyt. Journ.*, 1870, cxcv., 364) states that with proper precautions nitroglycerin can be heated to 193° C. without explosion.

Investigations by the Authors.

Apparatus Used.

As a part of the equipment of the explosives laboratory of the Bureau of Mines, there has recently been constructed, from designs made by the authors, a protective cabinet for the purpose of facilitating the study of explosive reactions. The cabinet, 76 cm. (30 inches) on a side, is made of steel plates 1·9 cm. (0·75 inch) thick. Means are provided for illuminating the interior of the cabinet, and a window of very heavy plate glass is so arranged as to permit observations being safely made of any work that is being conducted in the cabinet.

A number of experiments, intended mainly to test the resistance of the cabinet to explosive shock, showed observation to be perfectly safe through the protected window when a 2 to 3 grm. quantity of nitroglycerin exploded.

The illumination of the interior of the cabinet was effected by means of a 16-c.p. incandescent electric light. When lighting from without the chamber of the cabinet was desirable an electric light was placed in the dome of the cabinet, this dome being separated from

* *Technical Paper* 12, Bureau of Mines, Washington.

the chamber of the cabinet by a window of heavy plate glass, reinforced by a steel frame. The purpose of the dome was to prevent pieces of glass from this window from being a source of danger in the event of the window being ruptured. In many experiments a better illumination than was afforded by light admitted through the window in the top of the cabinet was desirable. Such illumination was obtained by an incandescent lamp within the chamber of the cabinet, the lamp being held in proper position by a suitable stand. With this method each explosion naturally resulted in the loss of an electric-light bulb, but the superior illumination compensated for the small cost of the broken bulbs.

The heavy plate glass of the windows was so greatly scarred after each explosion as to seriously impair its transparency. As the glass was exceptionally heavy, and therefore expensive, a means was sought by which the replacing of the heavy panes might be avoided. Complete success was obtained by placing a thin pane of ordinary glass, cut to the size of the window, on the inside of the cabinet and in contact with the plate glass. After each explosion it was only necessary to remove the pane of thin glass, which had become badly scarred, and to replace it by a new one. Thus, at a cost of one or two cents for each shot, a fully transparent window was provided.

As this cabinet seemingly offered an ideal means of conducting work that could not with any degree of safety be carried out by means heretofore at the command of experimenters, some studies were undertaken to determine the effect of temperatures between 100° and 200° C. upon pure nitroglycerin. In these experiments, to obviate the difficulties encountered by former investigators in regard to indirect measurements, such as those depending upon the distribution of heat along a metal bar, direct determinations of temperature were made, either by a thermometer that was immersed directly in the nitro glycerin under test and was observed through the plate-glass window, or by means of a thermocouple that was immersed within the nitroglycerin and was read by means of a galvanometer situated at such a distance as to be unaffected by the jar caused by the explosion.

Preliminary experiments showed that the measurement of temperature by means of the immersed thermocouple could be carried out very conveniently and with great precision. The thermocouple used was that which is commonly known as the "constantan-copper" thermocouple, one of the wires being composed of the alloy known as "constantan," and the other being of ordinary copper. Such a thermocouple is very sensitive, the wires are cheap, and after each explosion it is a very simple matter to solder together new portions of the wire to form a new junction, ready for standardisation.

In each experiment one junction of the "constantan-copper" thermocouple was immersed in the nitroglycerin under test, and the other junction of the thermocouple was wholly immersed in melting ice. The readings of the thermocouple were standardised by the use of liquids of known boiling point, liquids being selected that boil at about the same temperatures as were to be measured in the experiments.

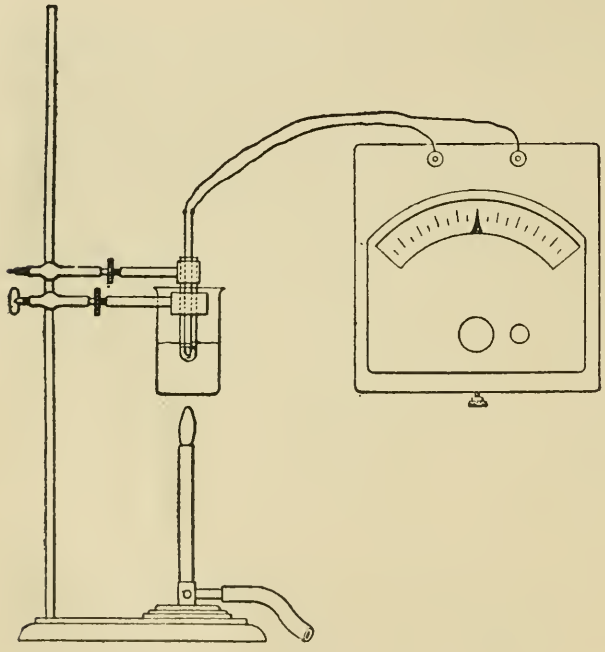


Fig. 1.—Apparatus for Determining the Explosion Temperature of Nitroglycerin.

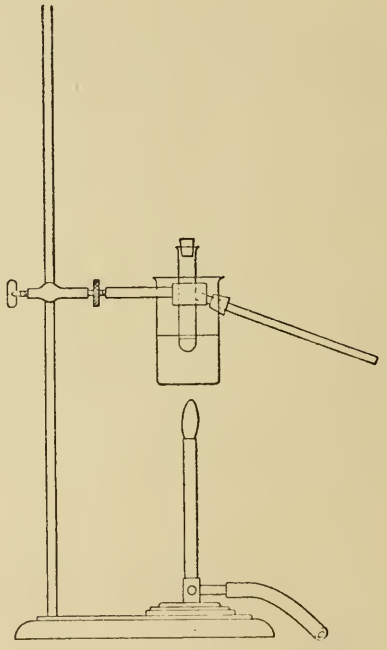


Fig. 2.—Apparatus Used in the Distillation of Nitroglycerin.

The Method of Procedure.

The method of procedure used in the study can be best explained by a general outline of some of the tests made. Usually about 2 cc. of nitroglycerin was taken, and was placed in a small test tube, held by means of a clamp in the proper position in a bath of melted paraffin. The thermocouple was placed in the nitroglycerin, and carefully adjusted in such position that the junction of the two wires was about in the centre of the nitroglycerin. The arrangement of the thermocouple, test-tube, and paraffin bath is shown in Fig. 1. The entire apparatus was then placed within the protective cabinet, and readings of the galvanometer were taken at intervals of 30 seconds.

All the changes that occurred were noted by an observer at the protected window of the cabinet, and by means of two watches carefully adjusted to run synchronously the observer at the cabinet and the observer at the galvano-

meter obtained continuous records of all the successive phenomena in the course of the experiment.

Changes Observed.

In the experiments with nitroglycerin no change was observed until the temperature of the nitroglycerin reached about 135° C. At this point the nitroglycerin became slightly more yellow in colour, and as the temperature rose a rapid deepening in colour was noted, until at about 140° C. the nitroglycerin was of a reddish-orange colour. At about 145° C. ebullition began; small bubbles formed in all parts of the nitroglycerin and rose in a regular manner. Generally foam collected over the top of the nitroglycerin at this stage of the heating, and copious red fumes were given off. From the phenomena described it will be seen that, although the ebullition in every way resembled true boiling in appearance, it was really very different in nature. Nitroglycerin seems to decompose at this temperature (145° C.), and the decomposition is accompanied by the vaporisation of undecomposed nitroglycerin. When the heating was continued, the temperature of the nitroglycerin steadily rose instead of remaining constant, as would have been the case if the phenomenon represented true boiling. Ebullition continued to become more and more active, and the evolution of reddish-brown fumes increased. At the temperature of approximately 218° C. the nitroglycerin exploded.

Effect of Heating at Constant Temperature.

After one or two experiments of the type just described had been reviewed, it seemed to be of interest to determine what effect would be produced upon nitroglycerin by keeping it in active ebullition for some time at a temperature just sufficient to maintain this condition. Accordingly, about 2 cc. of nitroglycerin was heated gradually until ebullition resulted; the heat was then regulated so as to maintain gentle ebullition for about thirty minutes, the flame under the paraffin bath being adjusted so as to keep the temperature of the nitroglycerin practically constant. Determinations by the nitrometer showed that nitroglycerin that had been treated thus for some time had a much lower nitrogen content than the original nitroglycerin. To determine as fully as possible the extent to which decomposition without explosion could be brought about in nitroglycerin maintained at a temperature between that at which ebullition begins and that at which detonation takes place, the apparatus shown in Fig. 2 was used. Several cc. of nitroglycerin was placed in the small fractionating tube therein shown. The temperature of the paraffin bath was increased until active ebullition began, and was then maintained at this point for about forty-eight minutes. As a result, a small amount of distillate collected in the receiving tube. This distillate and the residual nitroglycerin in the distilling flask were then collected and carefully examined.

The original nitroglycerin showed a nitrogen content of 18·45 per cent, whereas the residue left in the distilling flask, after being heated forty-eight minutes, showed a nitrogen content of 10·56 per cent. The distillate that collected in the receiving tube was observed to separate into two layers, one seemingly consisting of nitroglycerin and the other mainly of dilute nitric acid. The distilled nitroglycerin was carefully separated from the acid water. It was found to be of a bright green colour and to be actively giving off nitrous fumes. At the expiration of about half an hour the distilled nitroglycerin ceased giving off nitrous fumes and became almost colourless. It was then washed with dilute sodium carbonate solution and with water, dried in a desiccator, and tested in the nitrometer. It showed a nitrogen content of 13·5 per cent. Tests made by heating this distilled nitroglycerin in a free flame and by percussion upon an anvil showed it still to be violently explosive. The undistilled residue left in the distillation tube possessed only very weak explosive properties, thus showing the extent to which the decomposition of the nitroglycerin had proceeded.

Preliminary experiments having shown that nitroglycerin could be heated to a temperature of 200° C. for considerable periods of time without explosion, it became necessary to determine why some of the former investigators had found that the explosion point of nitroglycerin was so much below this temperature. Careful experiments by Hagen (Escales, "Die Explosivstoffe," iii. 160), carried out by immersing tubes containing nitroglycerin in a paraffin bath, the temperature of which, carefully tested by a thermometer, was 183·7 C., led to the belief that explosions were invariably brought about at this temperature. In the present series of experiments, however, in no case did nitroglycerin explode at a temperature below 200° C. Accordingly a very wide discrepancy is here apparent, for which an explanation should be found.

In the experiments made in heating nitroglycerin it was noted in many cases that the temperature of the nitroglycerin, as measured by the thermocouple, often continued to rise for a considerable length of time after the source of heat had been removed from beneath the paraffin bath. As the "lag" thus shown seemed to be far greater than could be accounted for by the transfer of heat by convection from the paraffin bath to the immersed tube containing nitroglycerin, it seemed probable that the decomposition of nitroglycerin, as evidenced by the ebullition taking place at temperatures above 145° C., was in reality a strongly exothermous reaction, and that therefore the tube of nitroglycerin might, in many experiments, be giving out heat to the bath instead of taking heat from it. To obtain definite information upon this interesting point, several experiments were carried out, in which the temperature in the paraffin bath and the temperature within the tube of nitroglycerin were simultaneously measured over a considerable range. It was found, as had been suspected from previous experiments, that the ebullition of nitroglycerin marks a form of decomposition which is accompanied by the evolution of much heat, and a tube of nitroglycerin immersed within a paraffin bath may attain a final temperature many degrees higher than the bath itself.

In one set of experiments a paraffin bath was heated to a definite temperature (164° C.), and the heat was so adjusted as to keep the bath at this temperature. A tube containing nitroglycerin (both the tube and the contained nitroglycerin being at room temperature) was then suddenly placed within the bath. The observations in this experiment are given in Table I.

This experiment clearly proved the fact that the temperature of nitroglycerin contained in a tube kept in a bath at a temperature sufficient to initiate and maintain the active decomposition of the nitroglycerin, may rise many degrees higher than that of the bath by which the tube is heated. Hence all former results obtained by placing nitroglycerin in baths of paraffin or other substances and noting the temperature of the bath when the explosion occurred are practically without value.

Effect of Heating at Rising Temperature.

In the experiment just outlined the amount of nitroglycerin taken (about 2 cc.) and the initial temperature of the bath (164° C.) were so adjusted that the maximum temperature reached by the nitroglycerin (180° C.) was below the temperature at which detonation would be brought about. A second experiment was made with the initial temperature of the paraffin 80° C. at the time the nitroglycerin was introduced, and with a flame under the paraffin bath sufficient to cause the temperature of the bath to increase rapidly. In this experiment also it was found that the maximum temperature reached by the nitroglycerin was many degrees higher than that of the bath by which it was being heated. The reading of the thermometer in the nitroglycerin at the instant before explosion occurred was 215° C., this being about the same temperature that had been previously noted in other experiments as the temperature at which the explosion of nitroglycerin was invariably brought about, the explosion

Table I.—*Result of Heating Nitroglycerin in a Bath at Constant Temperature.*

Temperature of bath. °C.	Temperature of nitroglycerin. °C.	Observations.
164	20	Tube containing nitroglycerin placed in bath. The temperature of the nitroglycerin rapidly rose, while the temperature of the paraffin bath dropped because of the transfer of heat from the paraffin to the cold tube and the nitroglycerin.
158	143	Ebullition of nitroglycerin began.
158	157	Violent ebullition.
160	163	
162	170	
163	173	
164	175	
165	177	
166	178	Nitroglycerin began to be thick and viscous.
167	179·5	
167·5	180	
167	178	
166	174	
165	171	
161	163	Total time of heating: 1 hour, 25 minutes. Sample converted to thick tarry dark brown mass.

Table II.—*Results of Heating Nitroglycerin in a Bath at Rising Temperature.*

Temperature of bath. °C.	Temperature of nitroglycerin. °C.	Observations.
80	49	Started heating nitroglycerin.
120	87	
150	120	
174	143	Ebullition of nitroglycerin began.
186	165	Violent ebullition.
190	175	
193	185	Nitroglycerin thick and viscous.
196	190	
196	195	
198	205	
201·5	215	Violent detonation. (Total time of heating, 5 minutes.)

temperature in a series of experiments having been found to vary from 215° to 222° C. The notes of the experiment just mentioned are given in Table II.

Several experiments having shown that nitroglycerin may become much hotter than the bath by which it is being heated, and that the bath temperature does not indicate the explosion temperature of nitroglycerin, a number of experiments were made in which nitroglycerin was heated in tubes that contained in some cases a carefully calibrated thermometer and in other cases a "constantan-copper" thermocouple. In all of the experiments thus carried out the results were almost uniform, the temperature at which ebullition began in nearly all the experiments being within two degrees of 145° C., and the temperature at which explosion occurred in all of the experiments being within two or three degrees of 218° C.

Summary.

The results obtained through the series of experiments here outlined may be thus summarised:—

Nitroglycerin begins to decompose at temperatures as low as 50° or 60° C. At a temperature of 70° C. nitroglycerin of commercial quality evolves enough nitrous fumes to give a decided test with potassium-iodide-starch paper at the expiration of 15 to 30 minutes. Moreover, nitroglycerin tends, even at very low temperatures, to be somewhat volatile, and it is well known that even at ordinary room temperatures nitroglycerin loses slowly in weight through volatilisation. At somewhat higher temperatures both the decomposition and the evaporation of nitroglycerin increase. At a temperature of about 135° C. the decomposition of nitroglycerin is so rapid as to cause the liquid to become of a strongly reddish colour, owing to the absorption of the nitrous fumes resulting from that which is decomposed; and at a temperature of about 145° C. the evolution of decomposition products is so rapid that, at atmospheric pressures, ebullition begins, and the liquid "boils" strongly. This "boiling" is due in part to the evolution of decomposition products (mainly oxides of nitrogen and water vapour) and in part to the actual volatilisation of nitroglycerin itself.

The decomposition of nitroglycerin is accompanied by the evolution of much heat, and as soon as ebullition of a sample of nitroglycerin has begun, enough heat is generated within the liquid to rapidly raise the temperature of the mass, unless some means is provided for conducting away the heat evolved. At temperatures between 145° and 215° C. the ebullition of nitroglycerin becomes more and more violent; at higher temperatures the amount of heat produced by the decomposing liquid becomes proportionally greater, and at about 218° C. nitroglycerin explodes.

When nitroglycerin is maintained at a temperature between 145° and 210° C., its decomposition goes on rapidly, accompanied by much volatilisation, and under these conditions nitroglycerin may be readily distilled. The distillate consists of nitroglycerin, nitric acid, water, and other decomposition products. The residue that remains after heating nitroglycerin under such conditions for some time probably consists mainly of glycerin, with small amounts of dinitroglycerin, mononitroglycerin, and other decomposition products. These substances are far less explosive than ordinary nitroglycerin, and accordingly by heating nitroglycerin slowly it can be caused to "boil" away until the residue consists of products that are practically non-explosive. In a number of experiments nitroglycerin was thus heated, and a copious residue was obtained. By carefully raising the temperature this residue could be made to char without explosion.

All temperatures found in this study were determined by thermometers or thermocouples immersed directly within the nitroglycerin. When thermometers were thus used, only those that had been checked with known standards were taken, and in all cases a table of corrections was applied. When thermocouples were used, the readings were checked against similar readings of the boiling-points of liquids of known composition, such materials being selected for standardisation as boiled at approximately the temperatures being measured in the experiment.

The temperature at which ebullition of nitroglycerin begins at normal atmospheric pressure was found to be 145° C. This result is correct within one or two degrees, although different samples of nitroglycerin naturally have somewhat different ebullition points, depending upon acidity, length of time of storage, &c. The temperature at which explosion is brought about (218° C.) should be accurate within about five degrees, differences being due, not to the method of testing, but to the individual variations of different samples of nitroglycerin.

It is the purpose of the authors to extend this work to cover the behaviour of nitroglycerin when heated in the presence of normal constituents of dynamite, stabilisers, &c., and it is hoped that determinations may be made of the explosion points of a considerable number of organic nitrates and nitrosubstitution compounds.

NOTICES OF BOOKS.

Primer of Scientific Management. By FRANK B. GILBRETH. London: Constable and Co., Ltd. 1912.

THE author of this book recently contributed to the *American Magazine* a series of articles upon Scientific Management, and as a result hundreds of letters from business men in all parts of the world were addressed to him, asking for further information. The replies to these queries as to the methods and aims of Scientific Management are contained in this book. It is written in the form of question and answer, and, as is perhaps almost inevitable from its origin, it does more in the way of answering objections than describing the actual details of the scheme. But the author makes out a very strong case for himself, and if half what he claims for his system can really be gained by adopting it he is doing the public a noteable service by bringing it before them. He explains how his scheme is going to confer a double benefit upon the industrial world by increasing wages and decreasing the amount of labour by the elimination of waste and of unnecessary fatigue, and if he is rather indefinite in his statements, at any rate the book should arouse the curiosity and interest of the thoughtful working man as well as of the employer of labour.

The British Journal Photographic Almanac, 1913. Edited by GEORGE E. BROWN, F.I.C. London: H. Greenwood and Co.

THIS well-known work, although it has reached the fifty-second annual issue, has lost none of its vitality. It is full of up-to-date matters of interest and value; the practical contributions connected with the production of negatives and prints form a prominent feature. There is a valuable article by Captain Wheeler, F.R.P.S., on "Practical Methods of Telephotography," and many new "dodges" in manipulation will be found in the "Epitome." A very fine example of machine photogravure work is given on the front page. "The Village Smithy" is a first-class production, and Messrs. Vandyck, the printers, are to be congratulated upon their success. There is also an example of Autochrome reproduction by Oskar Trinkler, of the Carl Zeiss staff, that marks a distinct advance in this class of work. The advertisements, which are as voluminous as usual, will be found to relate to practically everything that can be obtained in the photographic world.

Whitaker's Almanac for 1913. London: Joseph Whitaker.

THE present volume contains articles connected with the National Insurance Act, and Labour Unrest in the World, Labour Conciliation in the British Dominions, and the Rates of London. The rest of the contents of this work are so well known that there is no need to call attention to them here, except to note that there are nearly 1000 pages of closely printed matter and every line is of value.

Das Erdöl und Seine Verwandten. "Petroleum and Allied Substances.") By Dr. HANS VON HÖFER. Third Edition. Braunschweig: Friedrich Vieweg und Sohn. 1912.

THIS book is volume IV. of the new edition of Engler's "Neues Handbuch der Chemischen Technologie," which has been greatly enlarged and widened in scope. It deals with the chemical and physical properties of petroleum, its occurrence, origin, and extraction, and gives an excellent account of petroleum and allied substances. Recent work is critically discussed in a very unbiassed and temperate spirit, and all statistics have been brought down as nearly as possible to the present date.

Le Développement de l'Industrie de l'Impression depuis l'Invention des Matières Colorantes Artificielles. ("The Development of the Printing Industry since the Invention of Artificial Dyes"). By M. E. NŒLTING. Paris: Bourse du Commerce, Rue de Viarmes. 1912.

IN this article, which is taken from the annual *Bulletin* of the Association Générale des Chimistes de l'Industrie Textile, the author gives a very interesting account of the growth and development of the Calico Printing Industry. He first describes its state in 1869, at the time of the discovery of fuchsine and its derivatives, giving a clear outline of the methods then employed and the dyes known. He then proceeds to trace the development of the industry to the present day, describing the discovery of the most important artificial dyes and recent methods of fixing them. Though he gives an outline of the subject, only the author contrives at any rate to touch upon most points of importance, and the article would be read with interest by the young chemist who is beginning the study of cotton dyeing.

Dizionario di Merceologia e di Chimica Applicata. ("Dictionary of Technology and Applied Chemistry"). By Prof. Dott. VITTORIO VILLAVECCHI. Third Edition. Volume II. Milan: Ulrico Hoepli. 1913.

VOLUME II. of the third edition of this useful dictionary of applied chemistry covers the letters N to Z, and also contains the index. All the data given in it have been carefully revised, and many additions have been made of products which have come into importance in recent years. The dictionary has no rival in the Italian language, and it will be an indispensable addition to the libraries of chemists and technical colleges.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clv., No. 23, December 2, 1912.

Photolysis of Different Classes of Sugars by means of Ultra-violet Light.—Daniel Berthelot and Henry Gaudechon.—The authors have investigated the action of ultra-violet light on 10 per cent aqueous solutions of different sugars—ketoses, aldoses, &c.; the degradation of these sugars gives as fundamental gases carbon monoxide and hydrogen in simple proportions; that is to say, the same gases as unite to give methyl aldehyde, from which the sugars and the hydrates of carbon are formed in nature.

Action of Caustic Potash on Cyclohexanol.—Marcel Guerbet.—When cyclohexanol, $C_6H_{12}O$, is heated to 230° with caustic potash, the two condensed alcohols, cyclohexanylcyclohexanol, $C_{12}H_{22}O$, and dicyclohexanylcyclohexanol, $C_{18}H_{32}O$, are formed. The former undergoes slight oxidation, giving cyclohexanylhexanoic acid, $C_6H_{11}—C_6H_{11}O_2$. Cyclohexanylcyclohexanone, $C_{12}H_{20}O$, can be obtained by oxidising the alcohol with chromic mixture.

No. 24, December 9, 1912.

Action of Acids on Uranous Oxide.—A. Colani.—When acids act on uranous oxide a chemical reaction takes place, and not simple solution, uranous salt and water being formed. The inverse reaction is impossible. Concentrated sulphuric acid acts rapidly on uranous oxide, and a large proportion of it is converted into the sulphate, which is almost insoluble in the acid. Dilute sulphuric acid has only a very slight action on the oxide. Uranous oxide dissolves slowly in hydrochloric acid, and the quantity

of oxide dissolved in a given time varies greatly with the method of preparation of the oxide.

Synthesis by means of Mixed Organo-zinc Derivatives. α-Polychlorinated Ketones. Constitution of Ordinary Trichloracetone.—E. E. Blaise.—Dichloracetyl chlorides very easily etherifies α-oxyisobutyric acid, and the dichloracetoxyisobutyric chloride when condensed with mixed organo-zinc derivatives furnishes the corresponding cycloacetols. The latter readily split up to give the α-dichlor-ketones. Ordinary trichloracetone, boiling at 172°, is 1.1.3-trichloro-propanone.

Etherification of Cyclanols by Aromatic Acids.—J. B. Senderens and Jean Aboulenc.—The catalytic etherification of the cyclanols in presence of sulphuric acid can be effected with aromatic acids as with the acids of the fatty series, provided that the carboxyl is not directly united to the radical, but is separated from it by one or more fatty chains. In the former case the aromatic acid takes no part whatever in the reaction, the only product being cyclene, $C_nH_{2n-1}OH = C_nH_{2n-2} + H_2O$.

Bulletin de la Société Chimique de France.
Vol. xi.—xii., Nos. 22, 1912.

Antiseptic Rôle of Sea-salt and Sugar.—L. Lindet.—The antiseptic action of salt and sugar solutions can be explained by supposing that the microbes readily undergo plasmolysis; they give up to the solution a portion of their constituent elements and thus become weaker and lose their reproductive power. The author has tested this assumption by determining the composition of samples of yeast before and after they have been left in contact with salt and sugar solutions of various concentrations, and has found slight diminutions in the quantities of nitrogen and phosphoric acid. The microscopic examination of the yeasts also reveals the fact that they have become less strong.

Influence of Pressure on Alcoholic Fermentation.—L. Lindet and L. Ammann.—A pressure of 3 atmospheres does not retard the development of yeast, and fermentation proceeds in exactly the same way whatever may be the pressure to which the yeast is subjected, at any rate up to 2·80 m. of mercury, the same quantity of alcohol being produced.

MISCELLANEOUS.

Royal Institution.—On Saturday, February 8, Prof. Sir J. J. Thomson begins a series of six lectures on "The Properties and Constitution of the Atom." The Friday evening Discourse on January 31 will be delivered by George M. Trevelyan, on "The Poetry and Philosophy of George Meredith, and on February 7, by Sir John Murray, on "Life in the Great Oceans."

Cold Storage and Ice Association.—A meeting will be held at the Royal Society of Arts, John Street, Adelphi, London, W.C., on Friday, January 31st, 1913, at 8 p.m., when a paper will be read on the subject of "An Investigation of the Inflammability of some Insulating Materials," by R. Balfour. To be followed by discussion.

The New Zealand Greenstone Company, of Westland, intend to lose no time in developing its valuable jade property, which was recently discovered. Already surveys are completed for the rope-line tramway and traction engine, and specifications for contracts, which will give employment to a large number of men, are in course of preparation.

American Standard Dictionary.—We have received from Messrs. Funk and Wagnalls, the publishers of the 1893 edition of the "American Standard Dictionary," specimen pages of a new edition that has been for some years in preparation and will be issued shortly. The earlier work is characterised by a high order of excellence, but in the new publication the subject matter has been entirely recast and greatly extended. Several novel features have been introduced, notably the inclusion of the whole of the matter under one vocabulary; there is no addendum or supplement; proper names, geographical names, and encyclopædic matter, are all found under one alphabetical index. As an aid to pronunciation two keys are used, the first a "new key," the so-called "scientific alphabet" proposed by the American Philological Association; the second is the old key generally used in textbooks and dictionaries. The illustrations in the specimen pages are exceedingly good, and an extensive series of coloured plates is promised; one plate of the "World's Famous Diamonds" gives full sized drawings of the most notable stones in existence, including the Cullinan diamond before and after cutting. The work will be highly appreciated by both English and American scholars, and we look forward with interest to the complete edition.

Institute of Chemistry.—Mr. W. J. A. Butterfield, M.A., Assoc.Inst.C.E., F.I.C., will deliver the second of two lectures on "Chemistry in Gas-Works," on Friday, January 31st, 1913, at 8 p.m., in the Chemical Lecture Theatre of University College. Professor Raphael Meldola, D.Sc., LL.D., F.R.S., President, in the Chair. *Syllabus.*—The bearing of the magnitude of gas-works operations on the work of the gas works' chemist; the correlation between the character of a town gas supply and the different uses to which the gas will be put; methods of investigating the fitness of different descriptions of gas for different uses; the chemical aspects of prevalent methods of manufacturing coal-gas and water-gas; the principles of construction and control of furnaces on gas-works; the impurities of crude gas and methods for their removal; the effect of impurities on works' plant and consumers' fittings; by-products of different processes of gas manufacture, their examination and their influence on the choice of process; how the cost of manufacture and the distributing charges affect the choice of the grade of gas which should be supplied; the degree of accuracy which is of practical utility in analyses for the control of the operations of gas manufacture; methods of investigating the efficiency and utility of appliances for the use of gas for heating, lighting, and other purposes; directions in which chemical research is called for; qualifications and training requisite in a gas-works' chemist.

MEETINGS FOR THE WEEK.

Monday, 27th.—Royal Society of Arts, 8. (Cantor Lecture). "Liquid Fuel," by Prof. Vivian B. Lewes.

Tuesday, 28th.—Royal Institution, 3. "The Heredity of Sex and some Cognate Problems," by Prof. W. Bateson, F.R.S.

—— Royal Society of Arts, 4.30. "The Wool Industry in the British Dominions," by C. E. W. Bean, M.A.

Wednesday, 29th.—Royal Society of Arts, 8. "Co-partnership," by Aneurin Williams, M.A., &c.

Thursday, 30th.—Royal Institution, 3. "Recent Research on the Gas Engine," by Prof. B. Hopkinson, F.R.S.

—— Society of Dyers and Colourists, 8. "Possibilities of a Standard Light and Colour Unit," by J. W. Lovibond. "Simple Method for Detecting Silk, Cotton, and Wool Fibres in Admixture in Textiles," by W. P. Dreaper.

—— Royal Society. "Formation of usually Convergent Fourier Series," by W. H. Young. "General Theory of Elastic Stability," by R. V. Southwell. "A Spectro-photometric Comparison of the Emissivity of Solid and Liquid Copper and of Liquid Silver at High Temperatures with that of a Full Radiator," by C. M. Stubbs. "New Analytical Expression for the Representation of the Components of Diurnal Variation of Terrestrial Magnetism," by G. W. Walker. "Investigation into the Magnetic Behaviour of Iron and some other Metals under the Oscillatory Discharge from a Condenser," by E. W. Marchant.

Friday, 31st.—Royal Institution, 9. "The Poetry and Philosophy of George Meredith," by George M. Trevelyan.

Saturday, Feb. 1st.—Royal Institution, 3. "Aspects of Harmony," by H. Walford Davies.

THE CHEMICAL NEWS.

Vol. CVII., No. 2775.

THE PERIODIC SYSTEM AND THE RADIO-ELEMENTS.

By ALEXANDER S. RUSSELL,
Carnegie Research Fellow of the University of Glasgow.

It has been recognised for some time by chemists that some of the longer lived radio-elements, such as radium, radium F, and radium emanation, have definite places in the ordinary periodic system of the chemical elements. It is the object of this paper to show that all the radio-elements, whose chemical properties have been investigated, may be placed in the periodic system.

The following are the facts regarding the chemistry of the radio-elements as at present known (see Soddy's "Chemistry of the Radio-elements," and Rutherford's "Radio-active Substances").

Uranium 1 and Uranium 2 are the top members of the chromium, molybdenum, tungsten group of bodies (Group VI. A). Uranium X, ionium, thorium, radio-thorium, and radio-actinium have been shown by the work of Keetman, von Welsbach, Fleck, and others to be chemically so similar to one another that it has not yet been possible for anybody, by any chemical method tried, to separate any one of these bodies from any other, or to effect a concentration of one of them in a mixture of any two in the least degree. Such elements will be referred to in this paper as non-separable elements.

The work of Marckwald, Soddy, and of Strömholm and Svedberg, has shown that mesothorium 1, radium, thorium X, and actinium X form another group of non-separable elements. The element actinium has been shown to be chemically very similar to lanthanum, and, since it is the only radio-element of long life that is similar to lanthanum, it is natural to expect that it is the missing top member of the scandium, yttrium, lanthanum group of elements Group III. A). The three emanations are members of the inert group of gases. The chemistry of radium A, thorium A, and actinium A has not yet been investigated owing to the short periods which they possess. Von Hevesy has shown that the three products, radium B, thorium B, and actinium B, are all electrochemically very similar. The same author has shown that radium C, thorium C, and actinium C are also electrochemically very similar. Radium D is well known to be non-separable from lead. Actinium D and thorium D are electrochemically very similar, but it is not yet settled whether or not they are chemically similar to radium D and lead. Fleck has shown in a paper, to be published in the *Journal of the Chemical Society*, that radium B, thorium B, and actinium B are not only very similar chemically to one another, but are very similar in properties to lead, resembling this element more than any other known element. He has shown also that radium C, thorium C, and actinium C are all chemically similar, and are very similar to bismuth. Mesothorium 2 has been shown by the same author to be very similar to actinium and lanthanum, and radium E to bismuth.

Radium F was shown many years ago by Marckwald to be the missing member of the selenium tellurium group. (Group VI. B). It is thus seen that with the exception of radium A, thorium A, and actinium A the chemistry of all the radio-elements is now known with more or less certainty.

Recently, it has been shown by J. Chadwick and the author that radio-actinium consists of two successive products. These products are described later in the paper.

F. Soddy in his recent book, "The Chemistry of the Radio-elements," was the first to point out that after an element had expelled an α-particle, the valency of the resultant product in many cases differed from that of the parent product by two. Thus, uranium, which is hexavalent, is transformed after expulsion of an α-particle into uranium X, which, being non-separable from thorium, has a valency of four. Again, ionium, which is tetravalent, is transformed after expulsion of an α-particle into radium,

Table I.—*Thorium Series.*

A. Radio-element.	B. Common element to which this is chemically most akin.	C. Group in Periodic System to which this element belongs.	D. Difference in group number of any two successive products.	E. Radiation expelled.	F. Calculated difference in group number of any two successive products.
Thorium	Thorium	IV.A			
			2	α	2
Mesothorium 1	Radium	II.A			
			1	Rayless	1
Mesothorium 2	Lanthanum	III.A			
			1	β	1
Radio-thorium	Thorium	IV.A			
			2	α	2
Thorium X	Radium	II.A			
			2	α	2
Thorium emanation	Xenon	O			
			4	2α	4
Thorium A	?				
			1	β	1
Thorium B	Lead	IV.A			
			1	$\alpha+\beta$	1 or 3
Thorium C	Bismuth	V.A			
Thorium D	Lead (?)	IV.A			

TABLE II.—*Actinium Series.*

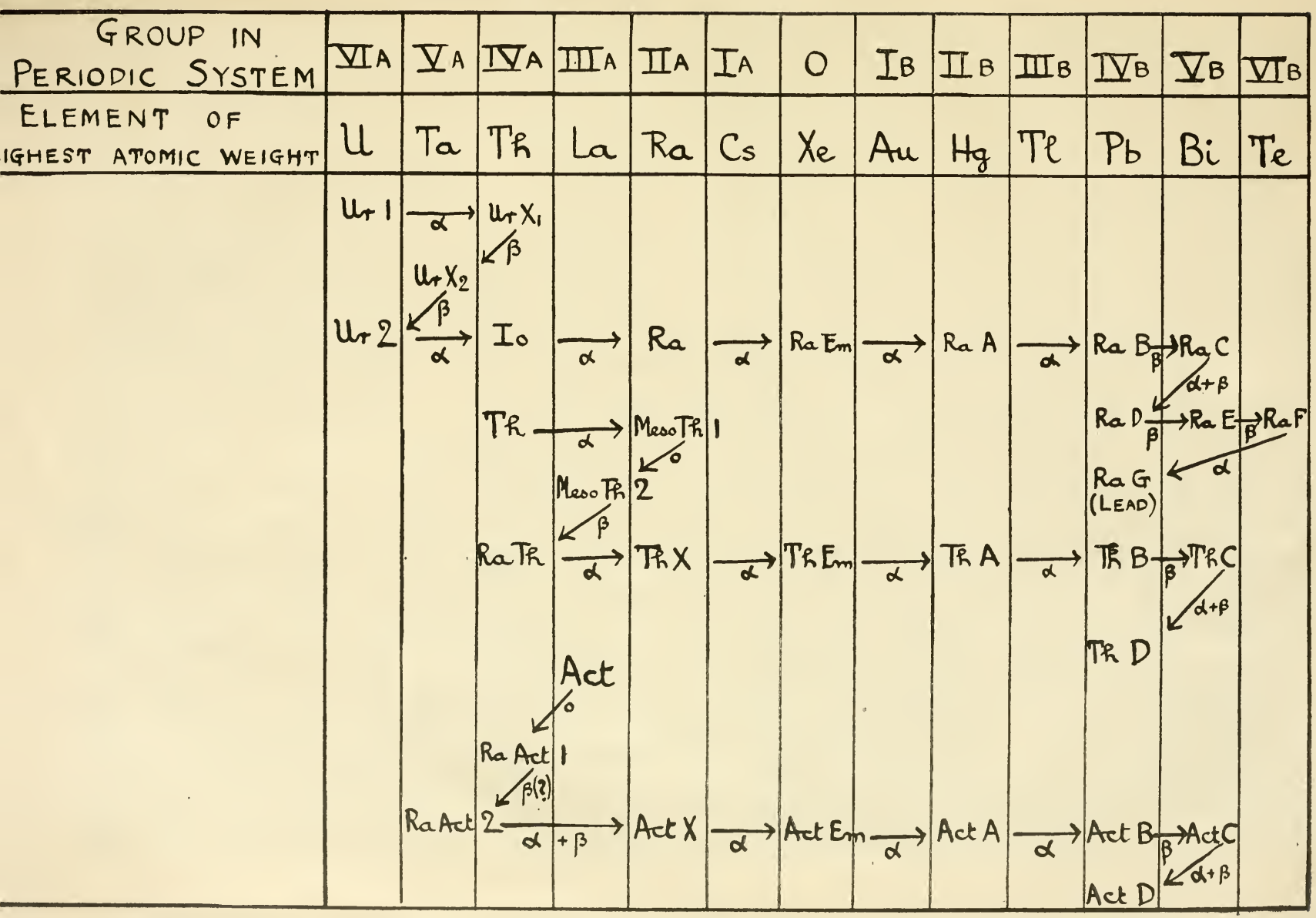
A. Radio-element.	B. Common element to which this is chemically most akin.	C. Group in Periodic System to which this element belongs.	D. Difference in group number of any two successive products.	E. Radiation expelled.	F. Calculated difference group number of any two successive products.
Actinium	Lanthanum	III.A			
			1	Rayless	1
Radio-actinium 1	Thorium	IV.A			
			2	Rayless	0, 2, or 4
Radio-actinium 2	?			$\alpha+\beta$	
			2		
Actinium X	Radium	II.A		α	2
			4		
Actinium emanation	Xenon	O		2α	4
			1		
Actinium A	?			β	1
			1		
Actinium B	Lead	IV.B		$\alpha+\beta$	1 or 3
Actinium C	Bismuth	V.B			
Actinium D	Lead (?)	IV.B			

TABLE III.—*Uranium Series.*

A. Radio-element.	B. Common element to which this is chemically most akin.	C. Group in Periodic System to which this element belongs.	D. Difference in group number of any two successive products.	E. Radiation expelled.	F. Calculated difference in group number of any two successive products.
Uranium 1	Uranium	VI.A			
			2	α	2
Uranium X_1	Thorium	IV.A			
			2	Rayless (?)	0 or 2
Uranium X_2	?			β	
			2		
Uranium 2	Uranium	VI.A		α	2
			2		
Ionium	Thorium	IV.A		α	2
			2		
Radium	Radium	II.A		α	2
			4		
Radium emanation	Xenon	O		2α	4
			1		
Radium A	?			β	1
			1		
Radium B	Lead	IV.B		$\beta+\alpha$	1 or 3
			1		
Radium C	Bismuth	V.B.		β	1
			1		
Radium D	Lead	IV.B		β	1
			2		
Radium E	Bismuth	V.B		α	2
Radium F	Tellurium	VI.B			
Radium G (lead)	Lead	IV.B			

which is bivalent. Radium, again, is transformed into the emanation which, being an inert gas, has a valency of 0. Further instances may be obtained in the thorium and actinium series. There are, however, certain exceptions to this rule as stated in this form, and further it does not apply to β-ray changes.

I have developed this fact pointed out by Soddy into the two following rules :—


Group in Periodic System
VI A
V A
IV A
III A
II A
I A
O
I B
II B
III B
IV B
V B
VI B
Element of highest atomic weight
U
Ta
Th
La
Ra
Cs
Xe
Au
Hg
Tl
Pb
Bi
Te
Ur 1
Ur X1
Ur X2
Ur 2
Io
Ra
Ra Em
Ra A
Ra B
Ra C
Ra D
Ra E
Ra F
Ra G (Lead)
Th
Meso Th 1
Meso Th 2
Ra Th
Th X
Th Em
Th A
Th B
Th C
Th D
Act
Ra Act 1
Ra Act 2
Act X
Act Em
Act A
Act B
Act C
Act D
α
β
α+β
β(?)

1. Whenever an α-particle is expelled by a radio-element the group in the periodic system, to which the resultant product belongs, is either two units greater, or two units less, than that to which the parent body belongs.
2. Whenever a β-particle or no particle is expelled, with or without the accompaniment of a γ-ray, the group in the periodic system to which the resultant product belongs is one unit greater, or one unit less, than that to which the parent product belongs.

These rules deal with the groups in the periodic system to which the radio-elements belong, not with their valencies. In this paper the valencies of the radio-elements are not considered at all. These rules do not apply to valency. (G. v. Hevesy has discussed this point in a paper to be published shortly in the *Philosophical Magazine*).

The validity of these two rules is tested in Tables I., II., and III. In Column A of each table is given the name of the radio-element; in Column B the common element to which this radio-element is most akin in chemical properties; in C is given the number of the group in the periodic system to which the element in B belongs. The nomenclature is that used in the ordinary arrangement of the elements in the periodic system, as given, for instance, in Nernst's "Theoretische Chemie," p. 185. In Column E is given the nature of the radiation expelled by the first of any two successive products. In D the actual difference in the group number of the two, and in F the difference in the group numbers of the two which ought to exist if the rules given above are strictly obeyed.

It is obvious that these rules can be put to a rigorous test only when we know the exact nature of the radiation or radiations expelled by each body, and also the exact chemical properties of each body. These data are most complete in the case of the thorium series, for, excepting lack of knowledge regarding the exact chemistry of thorium D and that of the quick changing product thorium A, the nature of the radiations from, and the chemical properties of, all the members of the series are known. It is essential, however, that the nature of the radiation expelled be known in every case, even though the chemical nature of the body is unknown. If the rules given are found to be strictly obeyed so far as exact data has been obtained, it is possible to predict the chemical properties of a radio-element provided its radiation is known. When a body like radium C expels both α-, β-, and γ-rays the group in the periodic system to which the resultant product belongs may, according to the rules, differ from that to which the parent product belongs, either by $2+1$ or $2-1$, *i.e.*, by 1 or 3.

Branch products are not considered in this paper, owing to the present uncertainty as to their exact chemical properties and to the nature of the radiation expelled by the body from which they are formed. The results for the thorium series are given in Table I.

It has been shown recently by J. Chadwick and the author (*Nature*, December 26, 1912, p. 463), that radio-actinium consists of two successive products, which will be referred to in this paper as radio-actinium 1 and radio-actinium 2. The first of these products expels either no rays or β rays only, and is similar chemically to thorium; the second expels α-, β-, and γ rays, and its chemical properties are at present under investigation. In the change from radio-actinium 1 to actinium X, therefore, there is at first a β-ray change, and then an α- and a β-ray change. According to the rules, therefore, the group to which actinium X should belong should differ from that to which radio-actinium 1 belongs by $1+2+1$, $1-2-1$, or $1-2+1$, *i.e.*, by 0, 2, or 4. The results for the actinium series are given in Table II.

The uranium series is ordinarily arranged as follows:—Uranium 1, uranium 2, uranium X, ionium, &c. There is, however, no experimental evidence at present against the view that uranium X lies between uranium 1 and uranium 2. Indeed, from analogy with the first part of the thorium series, it is to be expected that the series would run—Uranium 1, uranium X, uranium 2, ionium, &c. Since uranium X is chemically very similar to radio-actinium 1, and occupies in the uranium series the place that radio-actinium does in the actinium series, it is not impossible that uranium X consists also of two products, each of which expels in this case β-rays. If, therefore, we make the assumption, an assumption that is not contrary to any experimental evidence, that the series runs—Uranium 1, uranium X_1, uranium X_2, uranium 2, ionium, &c., the chemical properties of the products agree exactly with those to be expected from the rules. Until further work is carried out to show whether or not this is really the order of the elements in the disintegration series, this arrangement of mine must be considered speculative. All the products from ionium to the end product, however, agree exactly in their chemical properties with those to be expected from the rules given above. The results for the uranium series are given in Table III.

In Table IV. I have arranged the radio-elements in their places in the periodic system. In the top line of the table, the groups of the periodic system are arranged in descending order from VI. A to O, and in ascending order from O to VI. B. Under the name of each group is put the name of the common element of highest atomic weight belonging to that group. Under each of these elements are placed the radio-elements which are either chemically non-separable, or chemically most akin to it. I have placed uranium X and radio actinium 2 in group V. A, though at present the existence of the first, and the exact chemical nature of the second, is not yet known. These are the places in the periodic system that these elements should occupy if the rules given in this paper are true. Underneath the arrow joining any two successive products is given the name of the radiation expelled by the first. This table shows in a striking way the similarities of the three series.

This paper was written in August, 1912, and with the exception of that part dealing with radio-actinium has not been changed in any way. The results of Mr. Fleck, which are so useful in testing the validity of the rules given above, were obtained by him quite independent of this work, and the rules were found by me before I was acquainted with his results. I am indebted to him for allowing me to use his results.

I have to thank Professor Rutherford for the interest he has taken in this work.

Physical Laboratories,
The University, Manchester,
January 15, 1912.

Determination of Prussian Blue in Dyed or Weighted Silk or other Fibres.—H. E. Williams, F.C.S., and W. P. Dreaper, F.I.C.—Prussian blue can be determined in a weighted silk by converting the whole of the nitrogen into hydrocyanic acid, distilling it off into caustic alkali solution, and titrating the cyanide solution with standard silver nitrate. A weighed quantity of the silk is distilled with a convenient quantity of 10 per cent sulphuric acid and 0·1 grm. of pure cuprous chloride dissolved in a few drops of strong hydrochloric acid is added. The HCN distils over and is received in dilute caustic potash or soda, and then titrated with standard silver nitrate solution. The number of cc. of N/10 silver nitrate solution used multiplied by 0·00955 gives the amount of anhydrous Prussian blue, and if multiplied by 0·01355 will represent the actual weight of hydrated Prussian blue in the silk. Any insoluble or other dressing material and silk gum present must be removed by boiling for, say, half-an-hour in a 2 per cent sodium carbonate solution (or 1 per cent sodium carbonate and 1 per cent soap).—*Journal of Society of Dyers and Colourists*, xxviii., No. 11, 1912.

NOTES ON THE DIRECT VOLUMETRIC DETERMINATION OF TIN.*

By H. J. B. RAWLINS.

At a recent meeting of the Society of Chemical Industry, Mr. Ernest A. Lewis initiated a discussion on "Limits of Accuracy in Copper and Brass Analysis," and stated that, amongst others, the metal *tin* "cannot be determined accurately in the commercially pure state directly" (*Journ. Soc. Chemical Industry*, vol. xxxi., p. 96). Whilst most analysts would probably regard as an ideal figure the percentage of tin obtained as a difference from the direct determination of all impurities, they will nevertheless be forced in the usual routine of a busy laboratory to use a direct method. The impurities found in leading brands of the metal include, in varying quantity, antimony, arsenic, iron, lead, copper, sulphur, to mention only the more important: and a glance at these will emphasise the economic impossibility of submitting every sample to an exhaustive analysis in order to obtain a commercial estimate of purity.

Tin is now of such great interest, and the activity in the metal is so likely to increase, that it may not be inopportune to investigate what reliance may be placed upon the direct determination of the metal in a technical manner.

The estimation of tin in ores, slags, and other products has been the consideration of many able workers, who have elaborated convenient and accurate methods. These methods have been reviewed by L. Parry ("The Assay of Tin and Antimony,") and others, but, so far as the author can trace, no record has been made of attempts to utilise the delicate reactions of $SnCl_2$ in that critical manner of carrying out the iodometric method of copper assay which has yielded such valuable results (see, however, "The Volumetric Estimation of Tin by means of Potassium Bichromate," by H. Reynolds, CHEMICAL NEWS, xcvii., 13).

The experiments on which these notes are based were originally carried out to determine the relative convenience, with regard to accuracy and speed, of iodine and ferric chloride in the volumetric estimation of commercially pure tin, but they are directly related to the larger question, and, whilst presenting no striking features of novelty, it is hoped they will appeal to general interest. The two methods are now so widely utilised and detailed in all works of reference that description of their leading features is unnecessary.

The experiments fall under four headings:—

A. Preparation of solution of stannous chloride.
B. Titration with ferric chloride in excess, working back with titanium chloride.
C. Titration with ferric chloride alone.
D. ,, ,, iodine.

A. *Preparation of Solution of Stannous Chloride.*—The author has tried many methods to effect this by-no-means easy part of the operations. He found that, with suitable precautions, the stannous condition could be ensured from the start, thus eliminating the interference of reducers and saving much time and trouble. The process found to be most satisfactory was as follows:—

About 1 grm. of thinly rolled metal was placed, together with a lump of good white marble (about 3 grms. and free from coloured residue), in a 250 to 300 cc. flask, fitted with two leading tubes: one (0·8 cm. diam. passing about 2·5 cm. into the flask) opens out above into a small funnel-like enlargement, for introduction of acid and oxidiser; the other, of narrow bore, serves to connect to a similar flask by means of a rubber tube and small glass rubber-covered nozzle fitting into the funnel tube. In this manner a train of flasks was fitted up and the bulk of the air displaced by the passage of carbon dioxide. Each flask was then opened in turn at the funnel tube and 50 cc. concentrated hydrochloric acid poured in. The flask was immediately connected in the series and the quiet passage of carbonic acid gas maintained till solution was effected in the cold.

This arrangement proved quite easy to manipulate, and, although nearly all the solutions were obtained in the cold, several special series gave equally good results when the whole set was moderately warmed to hasten solution.

B. *Titration with Ferric Chloride in excess, working back with Titanium Chloride.*—The method adopted, the principles of which are described by E. Knecht and E. Hibbert ("New Reduction Methods in Volumetric Analysis," 1910, pp. 15 and 56), consisted in disconnecting the flasks successively and adding the $FeCl_3$ solution in slight excess from an automatic burette down the funnel tube; the excess of ferric salt being afterwards reduced by $TiCl_3$, using NH_4CNS as indicator.

Experiments showed that there was no necessity to warm the $SnCl_2$; in some cases this was done by partly immersing the flask in warm water before disconnecting from the CO_2 supply. It was found, however, to be much more satisfactory to complete the titration with $TiCl_3$ in the cold, as, although the indicator acted more sharply when warm, yet the intense red colour returned more quickly, and the end point became doubtful. With cold solutions, however, the end point was quite definite, and no reversible reactions were noticed for some time.

The exact strength of the $FeCl_3$ solution is a matter of no importance provided that it be in reasonable excess, the value of the $TiCl_3$ being determined in terms of $FeCl_3$, and, hence, of tin. The accuracy with which the automatic burette delivered the $FeCl_3$ solution is shown in the two sets of figures which were obtained by weighing successive deliveries from two different solutions of $FeCl_3$.

1.	103·435 grm.	1.	103·77 grm.
2.	103·425 ,,	2.	103·765 ,,
3.	103·430 ,,	3.	103·775 ,,
4.	103·420 ,,	4.	103·78 ,,
5.	103·420 ,,	5.	103·780 ,,
6.	103·425 ,,	6.	103·775 ,,

Both sets giving a maximum difference of about 0·015 per cent.

The delicacy of the end point between the $FeCl_3$ and $TiCl_3$ was examined by oxidising a solution of $Fe(NH_4)_2.2SO_4$ with $KMnO_4$ (Knecht and Hibbert, *loc. cit.*, p. 48), both in the absence and presence of fully oxidised $SnCl_4$, and found to be satisfactory. The value of the $TiCl_3$ was finally determined by titration of a solution of $SnCl_2$ oxidised with excess of $FeCl_3$, to which were added successive amounts of very carefully standardised $FeCl_3$ solution, with the following results:—

1000 cc. standard $FeCl_3$ contained 0·9495 grm. Fe'''
Therefore 1 cc. was equivalent to 0·0010 ,, Sn.

		$TiCl_3$	Mean.	Dif.
	150 cc. $FeCl_2.SnCl_4.FeCl_3$. "Blank"	11·45 11·30	11·38	—
a.	,, + 5 cc. standard $FeCl_3$	14·6 14·5	14·55	3·17
b.	,, +10 cc. ,, ,,	17·5 17·65	17·58	6·2

From *a.* 1 cc. $TiCl_3$, equivalent to 0·0016 grm. Sn.
b. 1 cc. ,, ,, 0·0018 ,, ,,

The following sets of trials performed with commerciall pure tin, with a negligible trace of antimony, indicate the uniformity of the processes, each set being, of course, independent, on account of slight variations in value of the $FeCl_3$ solutions.

In all these experiments the value of the $TiCl_3$ was 1cc. = 0·0016 Sn.

* A Paper read at a Meeting of the Institution of Mining and Metallurgy, December 19th, 1912.

	Tin, grm.	$TiCl_3$, cc.	$TiCl_3$, cc for 1·000 Sn.
A. *Tin Filings, Warmed; time of Solution about 45 minutes.*			
1.	0·9995	4·0	3·7
2.	,,	4·9	4·6
3.	,,	4·7	4·4
4.	,,	4·4	4·1
5.	,,	4·7	4·4

Maximum difference in terms of tin 0·14 per cent.

B. *Thin Strips, Warmed; time of solution about 90 minutes,*			
1.	0·9993	8·7	8·3
2.	0·9957	11·1	8·4
3.	0·9932	12·9	8·7
4.	0·9948	12·0	8·8
5.	0·9948	12·05	8·8
6.	0·9980	9·5	8·3

Maximum difference in terms of tin 0·08 per cent.

C. *Thin Strips, Cold; all Night.*			
1.	0·9988	8·65	7·9
2.	0·9989	9·3	8·6
3.	0·9986	8·8	7·9
4.	0·9961	10·9	8·5
5.	0·9972	10·1	8·4
6.	0·9954	10·9	8·1

Maximum difference in terms of tin 0·11 per cent.

In order to test whether the tin in the prepared solutions was within very narrow limits actually "stannous," a solution of $FeCl_3$ was prepared from the purest iron and acid in the cold, oxidised as far as possible by the gentle passage of air and finally at nearly a boiling temperature with H_2O_2. The solution so prepared was used to oxidise a special set of "Kahlbaum" tin trials, worked back with $TiCl_3$ as usual. Despite every precaution taken to ensure accuracy, such as weighing the whole solution of iron and the amount delivered from the automatic burette, the figures obtained appeared to indicate, not only that tin was not oxidised during its solution in the prescribed manner, but that the deficiency was on the iron side. The results, whilst being unsuitable for discussion, were of great regularity and indicated that a more refined series would confirm the stannous condition of the tin solutions.

The influence of antimony on ferric chloride is well known, and if present in more than the minutest trace, which is readily seen on dissolving the tin in cold acid, its presence must be duly allowed for. The influence of copper in small quantity on the $TiCl_3$ was tested and found to be practically negligible, as follows:—

Kahlbaum tin. Grm.	Copper. Grm.	$TiCl_3$. Cc.	$TiCl_3$ for 1·000 Sn. Cc.
0·9980	0·0005	6·2	4·95
0·9980	0·0005	6·0	4·75
0·9957	0·0010	7·6	4·95
0·9980	0·0010	6·0	4·75
0·9984	0·0025	5·7	4·7
0·9985	0·0025	5·6	4·7
0·9944	—	7·9	4·4
0·9965	—	7·0	4·8

(Collected results of estimations are recorded in tabular form later on.)

C. *Titration with Ferric Chloride.*—The process here was identical with the last series, except that the $FeCl_3$ delivered from the automatic burette was equivalent to less than 1 grm. of tin. Titration was then completed with dilute $FeCl_3$, using Cu_2I_2 and starch as indicator. The practical determination of the value of the dilute $FeCl_3$, under the conditions of an estimation, was ascertained by the titration of different weights of Kahlbaum tin with the strong $FeCl_3$, followed by the dilute solution. This value was found to be rather less than the theoretical when a dilute solution of $FeCl_3$, standardised for ferric iron, was used. The tin equivalent of the ferric iron was used as the factor in the absence of any better independent method of control. The end point appeared to be sharp, but not so sharp as one usually associates with iodine and starch reactions. The following illustrate the uniformity obtained (all dissolved cold) 1 cc. dilute $FeCl_3$ equivalent to 0·002 grm. Sn:—

Tin (grm).	Dilute $FeCl_3$ (cc.).	Dilute $FeCl_3$ for 1·000 Sn
0·9995	3·00	3·25
0·9994	2·75	3·05
1·0008	3·85	3·45
0·9993	2·5	2·85
0·9998	2·6	2·70

Maximum difference in terms of tin 0·15 per cent.

D. *Titration with Iodine.*—Two solutions of iodine—strong and dilute—were substituted for ferric chloride in this set of experiments. The value of the dilute solution being obtained by the careful solution of varying weights of pure tin and titration direct with starch as indicator.

Tin (grm.).	Dilute Iodine (cc.).	1 cc. dilute Iodine equivalent to Sn.
0·0382	15·25	0·0025
0·0404	16·2	0·0025
0·0960	38·5	0·0025

A test of uniformity of delivery of iodine from automatic burette gave:—

102·845 grm.	102·865 grm.
102·865 ,,	102·875 ,,
102·875 ,,	102·880 ,,

(NOTE.—The volume of iodine solution delivered may be rendered more uniform by making the solution with about 10 per cent of industrial spirit. This has not been found to introduce any secondary reactions.)

Before adding the strong iodine, 50 cc. of distilled water containing a little Na_2CO_3 is introduced into the flask, generating CO_2 and neutralising to a small degree the strongly acid liquor. (Further experience has shown it to be better to dilute with cold boiled distilled water saturated with CO_2.). The regularity of reaction is shown below; all solutions were obtained in the cold. 1 cc. dilute I_2 equivalent to 0·0025 grm. Sn.

Tin (grm.).	Dilute I_2 (cc.).	Dilute I_2 for 1·000 Sn.
0·9968	19·2	20·5
0·9954	18·7	20·5
0·9950	18·6	20·6
1·0002	20·6	20·5
0·9996	20·0	20·2
0·9980	19·7	20·5

Maximum difference in terms of tin 0·10 per cent.

Some of the results obtained by the three methods with certain brands of the metal are tabulated below. With every set of estimations one or more "checks" of Kahlbaum tin were carried through, the percentage of tin being obtained from the difference in the quantity of dilute solution required to complete the various titrations calculated for 1 grm. and reckoning the standard as "pure."

	Ferric and Titanium Chlorides.	Ferric Chloride.	Iodine.	Antimony.
	Per cent.	Per cent.	Per cent.	Per cent.
China tin ..	99·54	99·66	99·59	0·05
	99·62	99·46	99·62	
	99·58	99·39	99·52	
Billiton	99·94	99·80	99·90	Nil.
	99·84	99·95	99·91	
	99·92	99·94	99·96	
English refined	99·85	99·84	99·88	Minute trace.
	99·86	99·66	99·85	
	99·84	99·88	99·90	

All the foregoing experiments were conducted with tin containing only the smallest traces of antimony. This metal, by acting upon the excess of $FeCl_3$ in method 1, and more slowly upon the $SnCl_4$ in methods 2 and 3, would greatly increase the percentage of tin found. The author thinks, however, that the combination of the amount of dilute solution required to complete the reactions when antimony is present, with the direct determination of the antimony, may suffice to determine the tin. In support of this suggestion the figures obtained with a sample of tin-foil may be quoted. The foil was dissolved in the usual manner, leaving a heavy black residue which on adding excess of $FeCl_3$ completely dissolved, and the titration was finished with $TiCl_3$.

1 cc. of $TiCl_3$ was equivalent to 0·0016 grm. Sn, and therefore equivalent to 0·00065 grm. Sb, assuming that the latter is fully oxidised when present in so small a quantity. The foil was found, by separation and titration with $KMnO_4$, to contain 0·69 per cent Sb.

Titanium titrations of the tin-foil and "checks":—

Kahlbaum tin.	$TiCl_3$, cc.	$TiCl_3$, cc. for 1·000 Sn.
0·9980 grm	6·4	5·2 } mean 5·3.
0·9974 ,,	7·0	5·4 }

Tin foil (grm.).	$TiCl_3$ (c.c).	$TiCl_3$, cc. for 1·000.	Add $TiCl_3$ equivalent to Sb 10·66(cc.).	Diff. from check.	Sn (per cent).
0·9989	2·5	1·8	12·4	7·1	98·86
0·9987	2·8	2·0	12·6	7·3	98·83
0·9981	2·9	1·7	12·3	7·0	98·88

A complete analysis of this foil gave:—Sb 0·69 per cent; As nil; Fe 0·25 per cent; Pb 0·084 per cent; Cu 0·025 per cent; S 0·021 per cent; Sn by difference 98·93 per cent.

The extremely finely divided antimony also affects the iodine end point by reacting even in the cold with the $SnCl_4$ produced, hence the reduction by antimony, used by some as a method of preparing the tin for titration, must be likely to give high results. With a knowledge of the percentage of antimony present, its effect may be adjusted by allowing the solution after adding the strong iodine to stand until the antimony has gone into solution, finally completing the titration with dilute iodine and subtracting the equivalent of the antimony present.

The experiments indicate that, with care in dissolving, the solution of tin was obtained in the stannous condition, and when titrated with iodine or ferric chloride against checks of pure metal, direct results of technical accuracy were obtained. Indeed, it is highly probable that these results were better than would have been arrived at by the rapid technical estimation of the impurities. It cannot be too strongly emphasised that air must be rigidly excluded during the solution of the metal in acid. The author has failed to obtain equally good results by many of the methods usually described for this process.

Antimony is the great objection, but is present in only the smallest quantity in many brands, and when present may be allowed for as suggested.

In conclusion, the author has to express his thanks to the Directors of Messrs. Johnson and Sons, Assayers, Ltd., for permission to publish these notes of work done in their laboratories; and to Mr. E. A. Rayner, their assistant chemist, for many suggestions and help in carrying out the experiments.

ON THE DENSITY OF SOLID SUBSTANCES, WITH ESPECIAL REFERENCE TO PERMANENT CHANGES PRODUCED BY HIGH PRESSURES.*

By JOHN JOHNSTON and L. H. ADAMS.

To many it may seem that a paper at this time on the density of solids is superfluous, in view of the large amount of work which has been done on this subject heretofore. But any one who studies the voluminous literature pertaining to the subject will find that our knowledge of the true specific gravity of many pure solid substances is still far from satisfactory; for the reason, namely, that the density of a solid is really much more an individual property of the particular sample of material used than a general property of the chemical substance. This is especially evident from the work of Kahlbaum, Roth, and Siedler on the specific gravities of certain metals (*Zeit. Anorg. Chem.*, 1902, xxix., 197 *et seq.*: *Verhandlungen der Naturforsch. Ges. Basel*, 1903, xv., 9). As an example, we may take copper, for which in the tables of Landolt-Börnstein-Meyerhoffer, we find the following densities given :—

	Density =
Copper, cast	8·300—8·921
Copper, wire	8·930—8·949
Copper, hammered	8·919—8·959
Copper, electrolytic	8·884—8·952

with a general mean value of 8·933. Now the very careful determinations of Kahlbaum gave for pure distilled copper the value 8·9326, which after pressing to 10,000 atmospheres for eleven hours had increased to 8·9377; which, in turn, diminished again to 8·9317 after one hour at 20,000 atmospheres pressure. From the foregoing, it is evident that the density of a substance so common as metallic copper is known only to the second decimal place at most, and that our knowledge of the density of the element copper is still less certain.

The above divergence is without doubt due to differences in the moleeular configuration of the metal as a whole; for example, to the presence in varying amount of some form differing from the usual. The uncertainty due to this cause can be excluded by studying the after effects of various factors on substances which crystallise well and without inclusions, and do not readily yield an amorphous or allotropic modification. Salts fulfil many of these conditions, and possess the further advantage that direct microscopic observation is a certain criterion of the actual homogeneity of the crystals. Such microscopic examination is necessary; for, as Retgers showed ("Determination of the Specific Gravity of Salts Soluble in Water," *Zeit. Phys. Chem.*, 1889, iii., 289), there are outstanding differences between the recorded values of the density of salts, which, while doubtless attributable in part to faulty experiment, result in the main from a lack of homogeneity of the material; that is, the differences found are due to the occurrence in the material of inclusions or of vacuoles in varying amount.

In view of these facts it was decided to test the after effect of high pressures on the densities of some well defined crystalline substances. Since, however, one effect of very high pressures in some cases is a partial comminution of the material, it was necessary to ascertain if a change in density follows the reduction of a substance to powder, especially as contradictory statements with reference to this question appear in the literature.

In the present paper we propose to discuss the effect of various factors upon the density of solids. Much of the material presented has been derived from the somewhat scattered papers referred to in the text; our excuse for recapitulating it here is that many of the facts observed, and the permissible conclusions to be drawn from them,

* From the *Journal of the American Chemical Society*, xxxiv., No. 5.

are apparently by no means generally known. Before proceeding to treat of the factors which may influence the real or apparent density of a solid, it is advisable to discuss the methods by means of which accurate determinations of the density of a solid may be made.

The Methods for the Determination of the Density of Solid Substances.

The more important of these are five in number :— (1) The volumetric method ; (2) by means of the volumenometer ; (3) the flotation method ; (4) by the method of Archimedes ; (5) by means of the pyknometer.

1. The volumetric method, as its name implies, consists in determining by direct measurement the volume of a definite weight of material ; but, owing to the difficulty of obtaining sufficiently perfect geometrical forms, this method is not applicable where the highest accuracy is desired.

2. As regards the use of the volumenometer for determining the volume and hence the density of a substance, several types of instrument have been described, but none of them are accurate to better than 0·1 per cent, and accordingly are insufficient for the purposes of the present investigation. We have constructed a modified type of the volumenometer described by A. Lo Surdo (*Sci. Abstr.*, 1907, x., 2; from *Nuovo Cimento*, 1906, xii., 41), the accuracy of which, we had hoped, would be 1 part in 10,000. This accuracy we have so far been unable to attain ; but until certain minor changes in the apparatus have been made, it will be impossible to make a definite report as to the precision attainable with this form of instrument.

3. The flotation method possesses certain advantages, especially for the mineralogist, since a small fragment of material suffices, and the determination takes only a short time ; on the other hand, its applicability is limited by the lack of transparent liquids of sufficient density. In this method a heavy liquid is diluted with a lighter liquid until a small piece of the substance to be investigated remains suspended in the liquid. The density of the solid is then, of course, equal to that of the liquid, which is obtained by means of the Westphal balance or by any other appropriate method (see, for instance, Merwin, *Am. Journ. Sci.*, 1911, xxxii., 425; also Andreæ, *Zeit. Phys. Chem.*, 1911, lxxvi., 491, who by the use of a dilatometer is able to obtain results of a high order of accuracy).

4. The method of Archimedes is well known. The most serious source of error is that caused by the action on the suspending wire of surface tension at the upper boundary of the liquid. This effect can be made very small, however, by using an extremely fine platinum wire previously coated with platinum black (*cf.*, Kohlrausch, *Praktische Physik*, xi. Aufl., p. 40). For metals or other materials, which may be put in compact form, this is perhaps the most accurate method of density determination. With a weight of metal of 50 grms., the error should not exceed 2 or 3 parts in 100,000, if attention is paid to the temperature of the liquid.

5. The principle of the pyknometer method is so well known that no description is required. It has at various times been proposed to use, as the pyknometer liquid, substances or solutions of high density in place of water in order to increase the accuracy of the results. Among the better known of the liquids which have been suggested are thallium ethylate, solutions of various borotungstates, and a solution of the double iodide of mercury and potassium. It has, however, been pointed out* that there is some important objection to the use of each of these as a pyknometer liquid, particularly so when used with metals. For salts or any substances soluble in water where the use of water is precluded, xylene is a very suitable liquid. It possesses the advantage that air bubbles are very easily removed from it; and while its rate of evaporation is greater than that of water, no serious error from this source need be apprehended.

In general the pyknometer method (using water or xylene as the liquid) or the method of Archimedes is the most suitable for accurate work ; we accordingly made use of these methods, the former for salts and other fragmentary material, the latter for metals. With the method of Archimedes, the temperature of the liquid was read to 0·1° in order to calculate the true density of the substance.

Determinations by the pyknometer method were made according to the procedure recommended by Day and Allen (Publication No. 31, Carnegie Institution of Washington, p. 55 ; *Am. Journ. Sci.*, 1905, [4], xix., 93 ; *Zeit. Phys. Chem.*, 1905, liv., 1 ; or see W. F. Hillebrand, U.S.G.S. *Bulletin*, ccccxxii., p. 48), except that the later measurements were made with a new type of pyknometer bottle, which was devised to obviate certain difficulties incident to the use (especially in the case of fine powders) of the usual type of bottle with tapered stopper. This type has been found so satisfactory in every respect that in all the later experiments we have used it altogether for coarse as well as for fine powders.

An Improved Form of Pyknometer for the Density of Solid Substances.

The essential feature of this new form, which is illustrated in Fig. 1, is the plane ground joint, between stopper and bottle. The neck is made fairly thick, partly for the

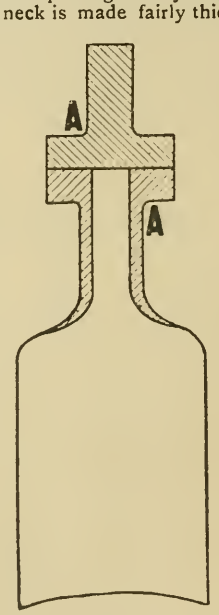


FIG. I.—IMPROVED FORM OF PYKNOMETER BOTTLE.

sake of strength, partly so as to minimise heat transfer when the bottle is held by the neck between the fingers. The two surfaces making up the ground joint should be *optically flat*, but not necessarily highly polished. Considerable care should therefore be exercised in grinding them properly, as the success or failure of the bottle depends upon the excellence of the joint. As a criterion of the quality of the joint, the stopper should be pressed forcibly on to the bottle with a slight rotary motion ; if the grinding has been sufficiently well done, the bottle may be lifted by the stopper. In making this test the stopper should be dry, that is, without grease or lubrication of any kind. Another requisite of success is that the pyknometer should be made in such a manner that no deep groove exists at A (see figure), or indeed that there be no recess from which excess of water cannot readily be wiped away.

* Kahlbaum, Roth, and Siedler, *Zeit. Anorg. Chem.*, 1902, xxix., 197—224. The reader, desirous of a full discussion of the accuracy of the various methods, is referred to this paper, and to a paper by J. W. Retgers, *Zeit. Phys. Chem.*, 1889, iii., 289.

(Note.—The bottles, which were made for us by the Emil Greiner Company, New York, were not entirely satisfactory as regards the grinding or freedom from grooves at the place indicated. However, by selecting two or three of the better ones, and grinding them further ourselves, we were able to obtain satisfactory results).

Pyknometers of this form have the following important advantages:—(1) The loss in weight by evaporation of the pyknometer liquid is negligible (for water it is of the order of 1 mgrm. in twenty-four hours). The pyknometer may therefore be allowed to stand in the balance case until temperature and moisture equilibrium is attained before it is weighed. (2) No grease or other lubricant is required on the joint; hence this obviates the uncertainty as to the weight of a variable, though small, amount of such grease. (3) Any small particles of grit or dirt which may accidentally lodge on the ground surfaces can be quickly and easily wiped off.

For these reasons this new type of pyknometer bottle gives considerably greater accuracy than the older forms; moreover, after very little practice its manipulation is quite as simple as with the older forms. After a few preliminary trials we were able to make successive fillings and weighings, both with water alone and with the sample plus water, which did not differ by more than 0·2 mgrm. This is illustrated by the following records, which are part of the results of an actual determination of the density of ground quartz which passed through a "200-mesh" sieve:—Weight of pyknomer filled with water at 25°, 29·6111 grms.; after refilling, 29·6112; weight of pyknometer and quartz filled up with water at 25°, 34·1957 grms.; after refilling, 34·1957; after standing eighteen hours in balance case, 34·1953.

In order to secure good results with this form of pyknometer it is highly important that attention be paid to the following details of manipulation:—The loosely-stoppered bottle is immersed in a thermostat, the temperature of which should be constant to 0·01°, to such a depth that the water-level is 2 or 3 mm. below the ground joint, and is allowed to remain at least fifteen minutes. Enough distilled water at the temperature of the thermostat is then poured into the bottle to fill it to overflowing (less than 1 cc. will usually be required). The neck of the pyknometer is then held firmly with one hand while with the other the stopper is pushed on firmly with a sliding and slightly rotary motion. While the pressure is still being maintained* the pyknometer is removed from the thermostat and wiped dry around the stopper with a soft cloth. The bottle may then be grasped by the neck and the wiping completed. It is advisable as a precaution to pass the corner of a piece of filter-paper around the stopper and top of the pyknometer in order to remove any drops of water which may adhere. After standing ten minutes (or more) in the balance case, the pyknometer is ready to weigh. (It is, of course, advisable to use a counterpoise). Great care should be taken not to heat it by the hand, or otherwise, while it is being wiped and removed to the balance case. If these directions are followed the stopper will adhere firmly and not fall off even if the bottle is turned upside down.

The Correction of Densities to Vacuum.

To all determinations of density which purport to be accurate a correction for the buoyancy of the air must be applied. The error due to this cause can be eliminated by making separate corrections on each of the weights involved in the determination; but it is much easier, and less liable to error, to make the correction to vacuum in one operation. This may be done by means of the formula given below, or by reference to Table I.; these results are applicable to any method in which density is measured by finding the weight of a certain liquid displaced by a given weight of the substance.

If s is the density of the substance as calculated from the uncorrected weights, S its true density, and L the true density of the liquid, then it can be shown that the vacuum correction to be applied to the uncorrected density, s, is $0{\cdot}0012\,(1 - s/L)$.

Let s = density of substance calculated from uncorrected weights
S = true density of substance
L = true density of liquid
W_s = uncorrected weight of substance
W_l = uncorrected weight of liquid displaced by substance

Then by definition, $s = LW_s/W_l$ . . . . . (1)

Assuming D to be the density of the balance weights, $W_s\,[1 + 0{\cdot}0012(1/S + 1/D)]$ and $W_l\,[1 + 0{\cdot}0012(1/L + 1/D)]$ are the true weights of the substance and liquid respectively (assuming that the weighings are made under normal atmospheric corrections so that the weight of 1 cc. of air is 0·0012 grm.).

Then the true density $S = \dfrac{W_s\,[1 + 0{\cdot}0012(1/S + 1/D)]}{W_l\,[1 + 0{\cdot}0012(1/L + 1/D)]}L.$

But from (1) $W_s/W_l = s/L$. Substituting this in the above we obtain utltimately $S = \dfrac{s + 0{\cdot}0012}{L + 0{\cdot}0012}\,L.$

Then the correction, $S - s = \dfrac{0{\cdot}0012(L - s)}{L + 0{\cdot}0012}$ . . . (2)

Since L is always large as compared with 0·0012 the denominator of the above expression may be taken as equal to L, making $S - s = 0{\cdot}0012(1 - s/L)$.

The values of $0\,0012(1 - s/L)$ for densities up to 20 and for liquids of density 1 (water), 0·852 (xylene), and 13·55 (mercury) are given in Table I.

(A table of the corrections when using water is given in Ostwald's *Lehrbuch der Allgemeinen Chemie*, 2 Aufl., I., p. 285; but the sign of the correction as given there is wrong).

It is to be noted that when the density of the substance is greater than that of the liquid (as is usually the case) the true density is smaller than the apparent or uncorrected density. In other words, the correction is negative and is therefore to be subtracted from the apparent density. All of the original results given in this paper have been corrected in this manner for the buoyancy of the air.

Table I.—*Vacuum Corrections for Density.*
Cor. = $0{\cdot}0012(1 - s/L)$.

Density of substance (s).	Correction: density of liquid = 1 (H_2O).	Correction: density of liquid = 0·852 (xylene).	Correction: density of liquid = 13·55 (Hg).
0·8	+ 0·00024	—	—
0·9	+ 0·00012	—	—
1	0·0000	− 0·0002	+ 0·0011
2	− 0·0012	− 0·0016	+ 0·0010
3	− 0·0024	− 0·0030	+ 0·0009
4	− 0·0036	− 0·0044	+ 0·0008
5	− 0·0048	− 0·0058	+ 0·0008
6	− 0·0060	− 0·0073	+ 0·0007
7	− 0·0072	− 0 0087	+ 0·0006
8	− 0·0084	− 0·0101	+ 0·0005
9	− 0·0096	− 0·0115	+ 0·0004
10	− 0·0108	− 0·0129	+ 0·0003
11	− 0·0120	—	+ 0·0002
12	− 0·0132	—	+ 0·0001
13	− 0·0144	—	0·0000
14	− 0·0156	—	0·0000
15	− 0·0168	—	− 0·0001
16	− 0·0180	—	− 0·0002
17	− 0·0192	—	− 0·0003
18	− 0·0204	—	− 0·0004
19	− 0·0216	—	− 0·0005
20	− 0·0228	—	− 0·0006

(To be continued)

* The purpose of this is to prevent the occurrence of a slight leak which may be caused by the apparent expansion of the liquid when the bottle is removed from the thermostat; this apparent expansion is due to the fact that under these circumstances the bottle cools slightly and contracts, while the temperature of the water remains practically unchanged.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, January 16th, 1913.

Sir ARCHIBALD GEIKIE, K.C.B., President, in the Chair.

PAPERS were read as follows :—

"*Effect of Junctions on the Propagation of Electric Waves along Conductors.*" By LORD RAYLEIGH, O.M., F.R.S.

"*Influence of Chemical Constitution upon Interfacial Tension and upon the Formation of Composite Surfaces.*" By W. B. HARDY, F.R.S.

It was shown by Dutré that when two fluids A and B are in contact the tension of the interface on T_{AB} is given by the equation $T_{AB} = T_A + T_B - 2T'_{AB}$.

The last term $2T'_{AB}$ is the work done by molecular forces when unit area of A is allowed to approach normally and come into contact with unit area of B. It is therefore a measure of the mutual action of A and B at the interface. Measurements of the tension of the surface between various fluids and water show that the quantity is determined by the chemical constitution of the fluids being smallest in the case of saturated substances, and largest for esters, alcohols, and acids.

Eötvos pointed out that in comparing the surface energy of different substances the comparison must be made between surfaces formed by an equal number of molecules. A remarkable feature of the relation of the quantity T'_{AB} to chemical constitution is that the concordance for members of the same chemical nature is for unit area, and not for the two-thirds power of the molecular volume, as Eötvos rule would lead us to expect. A direct interpolation of this unexpected fact in terms of the Young-Laplace theory of capillarity would make the range of molecular action vary inversely with the molecular volume of a fluid.

The chemically saturated substances examined do not spread over a clear water surface owing to the fact that the sum of the tension of the substance itself and of the interface is greater than that of water. At the same time the vapour of these substances will condense on to water.

The relation between the thickness of a film on water and the changes of tension and vapour pressure are considered at some length.

"*Duration of Luminosity of Electric Discharge in Gases and Vapours.*" By Hon. R. J. STRUTT, F.R.S.

"*Some Electrical and Chemical Effects of the Explosion of Azoimide.*" By Rev. P. J. KIRKBY, D.Sc., and J. E. MARSH, F.R.S.

1. The experiments consisted in exploding azoimide gas (HN_3) at low pressures between two insulated coaxial cylinders, of gilded brass, connected to the terminals of a battery of about 105 volts. The quantity of electricity that reached one of the cylinders was measured by a ballistic galvanometer and compared with the quantity of gas exploded. The results show that, in every case, the number of molecules of gas exploded was more than 100,000 times the number of pairs of gaseous ions observed. This disproportion indicates that the atoms of the gas when separated by the explosion do not carry electric charges. The gaseous ions are probably produced by favourable collisions of free atoms in the process of forming the products of the explosion. The electrical effects are obscured by inserting a resistance in the circuit.

2. The lowest pressure at which azoimide was observed to explode was 11 mm. This limit depends on the apparatus or on the method of explosion.

3. Azoimide is not absorbed by dry P_2O_5 but is rapidly absorbed by it when the P_2O_5 has taken up water vapour. This absorption is probably due to the action of phosphoric acid.

4. A deposit was found in the inside of the explosion chamber. This proved to be a transparent crystalline copper salt of azoimide, and it was explosive. Its crystalline character distinguishes it from the amorphous black powder formed by the exposure of copper or brass to moist azoimide. It had been formed by the series of explosions.

"*On Negative After-images with Pure Spectral Colours.*" By GEORGE J. BURCH, M.A., D.Sc., F.R.S.

The results obtained by Mr. A. W. Porter and Dr. Edridge-Green in their experiments on Negative After-images and Successive Contrast with Pure Spectral Colours, *Proceedings*, B, vol. lxxxv., p. 434, can be explained in accordance with the theory of Thomas Young if the "stray light" referred to by the authors is taken into account.

Thus fatigue by red light renders the blue and violet of a spectrum projected on a screen in an imperfectly darkened room darker and bluer along the line of the after-image, because it removes the red constituent of the "stray light" with which they are contaminated. The results of fatigue with other spectral colours may be similarly explained.

The effect of "lateral light," as he called it, on the after-image was well understood by Robert Waring Darwin, whose paper, published in 1786 in the *Philosophical Transactions*, was one of those on which Young's theory was based.

The phenomena of successive contrast with pure spectral colours in the absence of stray light were described by the author in the *Proceedings*, vol. lxvi., p. 204.

It is a matter of every-day demonstration in the laboratory that, to persons of normal colour sensation, spectral yellow changes to green after fatigue by red, and to red after fatigue by green. But persons whose green sensation is weak often fail to see it.

"*Factors Affecting the Measurement of Absorption Bands.*" By H. HARTRIDGE, M.A.

"*On a New Method of Measuring the Torque Produced by a Beam of Light in Oblique Refraction through a Glass Plate.*" By GUY BARLOW, D.Sc.

According to theory, the torque produced on a glass plate by the nearly normal passage of a beam of light is directly proportional to the angle of incidence and always tends to turn the plate further from the normal position. The period of small torsional oscillations of a plate suspended by a quartz fibre should therefore be increased when the plate is traversed by the light. An experiment is described in which this change in period, actually an increase of about $\frac{1}{2}$ per cent, was measured. The observed change agreed within 3 per cent with that calculated from theory.

"*Positive Ionisation Produced by Platinum and by certain Salts when Heated.*" By F. HORTON, D.Sc.

The emission of positive electricity from platinum and from several samples of aluminium phosphate and of sodium phosphate has been investigated at different temperatures, observations being made of the variation of the emission with time and with the pressure of the surrounding gas. It has been found that aluminium phosphate which has been prepared so as to be free from alkaline impurities gives a much smaller emission than the ordinary salt which contains these impurities. This confirms the observations of Richardson. The results of the experiments indicate that when the anode contains sodium, some of the positive ions consist of charged atoms of this element, and the similarity between this emission and the "anode rays" of Gehrcke and Richenheim is drawn attention to in the paper. A large thermionic emission can, however, be obtained in the absence of the alkali metals, and in these cases it appears to be due to gases emitted in an ionised condition by the heated anode. It is concluded that the positive emission from freshly heated platinum is due to this cause, and that with anodes containing a strongly electro-positive element like sodium, the

thermionic current is carried partly by atoms of that substance and partly by atoms or molecules of emitted gases.

"*On the Refraction and Dispersion of the Halogens, Halogen Acids, Ozone, Steam, Oxides of Nitrogen and Ammonia, and on the Causes of the Failure of the Additive Law.*" By Clive Cuthbertson and Maude Cuthbertson.

The refraction and dispersion of the elements and compounds named in the title have been determined between $\lambda = 6708$ and $\lambda = 4800$.

1. In hydrochloric, hydrobromic, hydriodic acids, sulphur dioxide, and sulphuretted hydrogen, the refractivity of the compound is less than the sum of the refractivities of the elements, and the dispersive power of the compound lies between those of its constituents.

2. In nitrous oxide, nitric oxide, ammonia, and ozone, the refractivity of the compound is greater than the sum of those of its constituents, and the dispersive power is greater than that of either constituent.

3. In steam the refractivity of the compound is less, and the dispersive power greater, than those of its constituents.

4. In all cases the change in dispersive power is great relatively to the change in refractive power.

5. In the case of the halogen acids, if the refractivity corresponding to one atom of hydrogen be deducted from that of the molecule, dispersion formulæ are obtained for the halogen *atoms* which show relationships with the corresponding formulæ for argon, krypton, and xenon, and with the critical temperatures of the halogens.

"*Liquid Measurement by Drops.*" By R. Donald, B.Sc. (N.Z.), D.P.H. (Oxf.).

To apply measurement by drops to various serological and bacteriological estimations of liquids and liquid suspensions, the author has worked out a system of using practically uniform easily-made pipettes of any size under any required constant pressure. The pipettes of suitably drawn-out glass-tubing are simply gauged in, *e.g.*, the Morse drill and wire gauge. The constant pressure is obtained by a column of mercury flowing as a piston to and fro in a suitable glass tube held at any required angle in a stand or, for less exact work, in the hand.

"*On the New Theory of Integration.*" By Prof. W. H. Young, F.R.S.

The present communication is a sketch of a mode whereby the modern theory of generalised, or Lebesgue, integration may be developed without the aid of the Theory of Sets of Points. The theory is built up step by step by means of monotone sequences from the consideration of the elementary functions tacitly employed in the classical treatment of the integration of continuous functions, and it is shown how Darboux's work forms a natural link between that theory and the most modern developments. The principle underlying the exposition is that a function must be said to have an integral if it can be expressed as the limit (finite, or infinite with determinate sign) of a monotone succession of functions, belonging to a class of functions whose integrals have already been defined, provided only that the limit of the integrals of the functions of every such succession is the same; this limit is then called the integral of the given function.

The key to the whole matter lies in the proof *by means of monotone sequences alone* that any bounded function which naturally presents itself, even one belonging to the most complicated type, is such that a *lu-* and an *ul*-function, having the same integral, can be found, between which the function itself lies. In Darboux's treatment an *l-* and a *u*-function are virtually employed, but these functions have not in general the same integral.

It is pointed out how the method leads *intuitively* to some of the chief theorems in the most modern theory. These are thus seen to be the mere translation into the new language of algebraical and other well-known elementary facts.

NOTICES OF BOOKS.

Manual of Chemistry. By W. Simon, Ph.D., M.D., and Daniel Base, Ph.D. Tenth Edition. London: Baillière, Tindall, and Cox. 1912.

Much fresh matter has been added to the tenth edition of this manual of chemistry, including discussions of thermochemistry, the ionic theory, &c. Moreover, certain new substances of medical interest have been included for description for the first time, such as sodium cacodylate, salvarsan, and atoxyl, and the section on physiological chemistry has been re-written. The manual provides a complete theoretical text-book, laboratory book, and work of reference for the use of the medical student, who, if he possesses it, should need no other book on chemistry or chemical physics. The information given in it is well selected and clearly expressed, and the new matter is in every respect well up to the excellent standard of the older parts of the book.

A Laboratory Manual in Chemistry. By William Conger Morgan, Ph.D. (Yale) and James A. Lyman, Ph.D. (Johns Hopkins). New York: The Macmillan Company. 1912.

This little book will be very helpful to teachers, and even if they do not use as their text-book the authors' "Chemistry," to which it is a companion volume, they will very probably find that it is well worth getting. The experiments described in it include some which every student should perform for himself, and others which are intended to be done by the demonstrator before the class. Many of them are novel and are striking enough to make considerable impression on the student. Complete lists are given of the apparatus and materials required by a class of ten. In the early parts of the book there seems to be a certain lack of sequence in the experiments, and the deductive powers and originality of the student are perhaps exercised hardly as fully as they might be, but on the other hand the course should certainly develop his powers of observation to their fullest extent.

The Freezing-Point, Boiling-Point, and Conductivity Methods. By Harry C. Jones. Second Edition. Easton, Pa.: The Chemical Publishing Co. 1912.

Although some account is given in this little book of the theoretical basis of the freezing and boiling point methods of determining molecular weight, and the freezing-point and conductivity methods of determining electrolytic dissociation, the author's chief aim, which he admirably fulfils, is to describe the actual laboratory methods of performing the experiments. He gives full directions, from which the student should be able to work with little or no outside help, and a few typical results are appended. In the second edition the boiling point method as applied to the measurement of electrolytic dissociation in non-aqueous solutions is described for the first time and some slight corrections have been made.

Trattato di Chimico-Fisica. ("Treatise on Physical Chemistry"). By Harry C. Jones. Translated into Italian by Dott. Michele Giua. Milan: Ulrico Hoepli. 1913.

This translation has been made from the fourth and last English edition of Prof. Jones's Treatise, with some few minor additions made by the translator, and Italian chemists will be glad to be able to read in their own language such an admirably clear and interesting account of the principles of physical chemistry. Dr. Molinari has contributed to the volume a short preface, in which he calls attention to the great importance of the study of physical chemistry, and the excellence of Prof. Jones's exposition of the subject.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Bulletin de la Société Chimique de France.
Vol. xi.-xii., No. 23, 1912.

Saturation by Iodine of the Ethylenic Bonds of Oleic Acid and the Molecular Magnitude of Dissolved Iodine.—J. A. Muller. -The determination of the limiting coefficients of reaction, at two different dilutions and at the same temperature, in the action of iodine on oleic acid, using carbon tetrachloride or ethyl acetate as solvent, gives a means of ascertaining the molecular magnitude of dissolved iodine. The results show that in both solvents at the ordinary temperature the molecules are composed of two atoms. Probably in carbon tetrachloride the iodine is present as free molecules, while in solutions in ethyl acetate the molecules are combined with those of the solvent.

New Nitro-compound of Cellulose.—M. Tassart.—If sulphuric acid and nitric acid are allowed to act in succession on cotton, any rise of temperature being prevented, a compound containing approximately 13·5 per cent of nitrogen (α-nitrocellulose) is obtained. It is a white, insoluble, unstable powder, which becomes pasty, gives off nitrous vapours, and finally catches fire when heated over the water-bath. If it is very carefully heated spontaneous ignition can be avoided, and the residue contains 6 per cent of nitrogen and reduces Fehling's solution. A mixture of α-nitrocellulose and diphenylamine, or glucose, or some other substances, simply chars when heated on the water-bath; no nitrous fumes are evolved nor does the mixture ignite. Other substances, such as paraphenylene-diamine, lower the temperature of ignition. α-Nitrocellulose is soluble in methyl and ethyl alcohols, aldehyde, acetone, &c.

Annales des Falsifications.
No. 48, 1912.

The Hübl and Wijs Methods of Determining the Iodine Index of Fats.—M. August.—If a solution of iodine containing 3·50 grms. of hydriodic acid per litre is used in the determination of the Hübl index the results obtained are accurate and comparable, whatever the age of the solution. The difference between the Wijs and the Hübl indices, when determined by means of an acid liquid, is very small, and with the majority of fats and oils does not exceed 1 per cent. The influence of temperature upon the two indices is negligible between 10° and 25°. An hour's contact is sufficient for the determination of the Hübl index for most fats. The Wijs method is both more rapid and less expensive than the Hübl method.

MISCELLANEOUS.

Institute of Chemistry. — *Pass List, December—January Examinations.*—Of twenty-seven Candidates who presented themselves for the Intermediate Examinations, held in Glasgow in December and in London in January, eight passed:—A. L. R. Clarke, B.Sc. (Lond.); G. N. Grinling; C. W. McHugo; H. A. Phillips; H. V. Potter; A. B. Stich. B.Sc. (Glas.); H. E. L. Thomas; and F. D. White. Of nineteen Candidates who presented themselves for the Final Examination, fifteen passed:—In the Branch of Mineral Chemistry—C. D. Barber, B.Sc. (Lond.); T. T. F. Cartwright, B.Sc (Lond), A.R.C S. (Lond.); R. M. Doidge, B.Sc. (Lond.); F. M. Potter, B.Sc. (Lond.), A.R.C.S. (Lond.); and J. A. Watson, A.C.G.I. In the Branch of Metallurgical Chemistry—F. G. Conyers. In the Branch of Organic Chemistry—K. C. G. Arbuthnot, B.A. (R.U.I.); J. C. Earl; and F. G. Tarn. In the Branch of the Chemistry of Food and Drugs, and of Water—J. W. Flint, B.A. (Cantab.); D. R. Frazer; H. E. Watts, Ph.D. (Zurich), B.Sc. (Lond.). For the Certificate—E. J. Wilson, M.A. (Cantab.), F.I.C. In General Chemistry—B. W. Drinkwater, A.R.S.M., A.R.C.S. (Lond.); and W. C. Ball, M.A. (Oxon.), Sc.D. (T.C.D.).

Society of Public Analysts.—The Annual General Meeting of the Society will be held on Wednesday, February 5th, at the Chemical Society's Rooms, Piccadilly, W., at 8 p.m. The Accounts for the year will be presented, the President will deliver his Annual Address, and the Election of Officers and Council for the ensuing term will take place. The Ordinary Monthly Meeting of the Society will be held immediately following the Annual General Meeting, when the following Papers will be read:—

"Antipyrine in Toxicological Analysis." by G. D. Lander, D.Sc., F.I.C., and H. W. Winter.

"The Accurate Determination of Carbon Dioxide in Carbonates," by Frank Sturdy Sinnatt.

"A New Method for the Volumetric Estimation of Chromium, Vanadium, and Iron in Admixture," by Frederick W. Atack, M.Sc.

"Note on Hardened Oils," by Arthur W. Knapp, B.Sc., F.I.C.

Dinner Club.—Members of the Society and their friends will meet to dine at Blanchard's Restaurant, Beak Street, Regent Street, W., at 6.15 p.m., when it is hoped that as many as possible will be present. Members of the Society who are not Members of the Dinner Club, but propose to attend on this occasion, are requested to notify the Hon. Secretary, Mr. L. MYDDLETON NASH, "Westlands," Princess Road, Finsbury Park, N., by postcard, of such intention, in order that adequate accommodation may be provided.

MEETINGS FOR THE WEEK.

MONDAY, Feb. 3rd.—Royal Society of Arts, 8. (Cantor Lecture). "Liquid Fuel," by Prof. Vivian B. Lewes.
— Royal Institution, 5. General Meeting.
— Society of Chemical Industry, 8. "Behaviour of Paint under the Conditions of Practice with Special Reference to the Aspersion cast upon Lead Paints," by H. E. Armstrong and C. A. Klein. "Technical Production of Ethane," by C. Sprent. "Feeding Value of the Horse Chestnut," by S. J. M. Auld

TUESDAY, 4th.—Royal Institution, 3. "The Heredity of Sex and some Cognate Problems," by Prof. W. Bateson, F.R.S

WEDNESDAY, 5th.—Royal Society of Arts, 8. "The Economic and Hygienic Value of Good Illumination," by Leon Gaster.

THURSDAY, 6th.—Roval Institution, 3. "Recent Research on the Gas Engine," by Prof. B. Hopkinson, F.R.S.
— Royal Society. "Influence of the Resilience of the Arterial Wall on Blood Pressure and on the Pulse Curve," by S. R. Wells and L. Hill. "Occurrence of a Ganglion in the Human Temporal Bone not hitherto described," by A. A. Gray. "Action of Adrenin on Veins," by J. A. Gunn and F. B. Chavasse. "Preliminary Report on the Treatment of Human Trypanosomiasis, and Yaws, with Metallic Antimony," by Capt. H. S. Ranken. "Further Researches on the Extrusion of Granules by Trypanosomes and on their further Development," by Major W. B. Fry and Capt. H. S. Ranken (with a note on Methods, by H. G. Plimmer).
— Chemical, 8.30. "Presence of Helium in the Gas from the Interior of an X-ray Bulb," by Sir W. Ramsay. "Presence of Neon in Hydrogen after the Passage of the Electric Discharge through the latter at Low Pressures," by J. N. Collie and H. Patterson. "Vaubel's supposed Phenyldiimine," by M. O. Forster and J. C. Withers. "Mode of Combustion of Carbon," by T. F. E. Rhead and R. V. Wheeler. "Latent Heat of Vapours," by M. P. Applebey and D. L. Chapman. "Some Derivatives of *o*-Xylene," by J. L. Simonsen.

FRIDAY, 7th.—Royal Institution, 9. "Life in the Great Oceans," by Sir John Murray, K.C.B., &c.

SATURDAY, 8th.—Royal Institution, 3. "The Properties and Constitution of the Atom." by Prof. Sir J. J. Thomson, O.M., F.R.S., &c.

THE CHEMICAL NEWS.

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RECENT PROGRESS IN ORGANIC ARSENIC COMPOUNDS.

By E. de BARRY BARNETT, B.Sc., A.I.C.

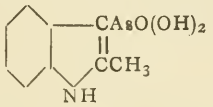
The first organic arsenic compound isolated was cacodyl oxide, which was obtained in the crude state by Cadet in 1760 by distilling sodium acetate with arsenic trioxide. The composition of the cacodyl compounds was fully elucidated by Bunsen in his researches on compound radicals (1837-1843). Although a considerable amount of work of organic derivatives of arsenic has been published from time to time, it is only during the last five years that anything like a systematic examination of them has been carried out. The sudden impetus given to the study of these compounds was due to the discovery by Ehrlich of their valuable therapeutic properties, especially in the treatment of diseases of protozoal origin, such as syphilis and sleeping sickness. For this purpose it is necessary to obtain a compound which, although it has a powerful effect on parasites, has but slight toxic properties for the host. One or two aliphatic compounds have been used in medicine, such as salts of cacodylic acid, Me_2AsOOH, and "Arrhenal" or "New Cacodyl," $MeAsO(ONa)_2$, but by far the greatest interest centres round the aromatic compounds, and it is only these that will be discussed in the following pages.

Nomenclature.—The usual nomenclature denotes acids of the types $RAsO(OH)_2$ and R_2AsOOH as arsinic acids. As this is very apt to lead to confusion the suggestion of Pyman and Reynolds, in which $RAsO(OH)_2$ is an arsonic acid and R_2AsOOH an arsinic acid, will be adopted. The arsenoxides have the structure RAsO, and the arseno compounds, which correspond to the azo-compounds, the structure RAs:AsR. The dihydroxyarseno-compounds correspond to the unknown hydrated azoxy-compounds and have the structure RAs(OH)(HO)AsR.

The Arsonic Acids.

Formation.—Bechamp (*Comptes Rendus*, lvi., I., 1172) obtained a compound by heating aniline with arsenic acid, which he regarded as arsenanilide. The sodium salt of this was introduced into medicine under the name of "atoxyl," but it was only in 1907 that its true constitution was discovered by Ehrlich and Bertheim (*Ber.*, xl., 3292). They found that it could not be hydrolysed, that it contains a primary amino-group which can be diazotised in the usual way, and that on treatment with hydriodic acid it gives *p*-iodoaniline. Hence Bechamp's substance must be regarded as *p*-amino phenylarsonic acid, and, from analogy to sulphanilic acid, it has been named arsanilic acid. The method of obtaining arsanilic acid, viz., by heating the arsenate of aniline, or better by heating a mixture of aniline and arsenic acid for several hours to 170-200°, is of very general application (*Ber.*, xli., 931, 1672; *Journ. Chem. Soc.*, xciii., 1893; D.R.P., 219210). The reaction is exactly analogous to that whereby sulphanilic acid is obtained, *i.e.*, by roasting the acid sulphate of the base, and the arsonic group invariably enters the *para*-position to the amino-group if this is free. If the *para*-position is occupied the arsonic group enters the *ortho*-position, but the yields are much poorer (*Ber.*, xlii., 3619). *p*-Nitraniline (*Ber.*, xliv., 3293; D.R.P., 243693) is exceptional, as when fused with arsenic acid it gives 2 amino-5-nitro-phenyl arsonic acid in good yield. If the *para*- and both *ortho* positions are occupied, no arsonic acid is formed. It is worth noticing that it has long been known that Magenta prepared by oxidising a mixture of aniline and *o*- and *p*-toluidine with arsenic acid always contains traces of arsenical impurities. Obviously these are arsonic acids. Phenols can also be arsonated by fusing them with arsenic acid, but the yields are very poor (D.R.P., 205616). The arsonic group enters the *para*-position to the hydroxyl group.

Some heterocyclic compounds can also be arsonated. Thus methyl ketol when warmed with an aqueous solution of arsenic acid gives an arsonic acid of the structure (D.R.P. 240793):—



Bart (D.R.P., 250264) has obtained arsonic acids by treating diazo-solutions with potassium arsenite in neutral, or better in faintly alkaline, solution. The reaction does not take place readily with diazo-salts made from unsubstituted amines (diazo benzene is expressly excepted in the patent) and the *iso*-diazotates react more readily than the normal salts:—

$$ArN{:}NX + K_3AsO_3 = ArAsO(OK)_2 + NaX + N_2.$$

The reaction can also be carried out by treating the diazo-solution with the arsenite in the presence of copper powder (*Pat. Anm. Kl. o. B.* 61146). Bart's method has proved extremely useful for obtaining arsonic acids which are unobtainable by the arsenic melt method, such, for example, as benzene-*p*-diarsonic acid (from arsanilic acid), *o* carboxybenzene arsonic acid (from anthranilic acid), &c. The exact conditions of the reaction require careful investigation, as Gutmann has examined the action of arsenites on normal and *iso* diazotates and apparently failed to detect any arsenical compounds, the chief reaction being the reduction of the diazo-group.

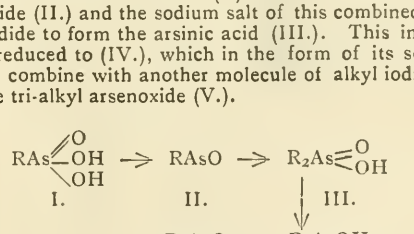
Bart's reaction also takes place when the arsenite is replaced by an arsenoxide, in this case an arsinic acid being formed:—

$$ArN_2X + Ar'As(ONa)_2 = ArAr'As{\leqslant}^{O}_{ONa} + NaX + N_2.$$

Arsonic acids can also be obtained by the action of an organic halogen compound on sodium, or better on potassium arsenite (*Ber.*, xvi., 1493; xliii., 925; *Annalen*, ccxlix., 147; *Journ. Am. Chem. Soc.*, xxviii., 347; xxxiii., 101):—

$$RI + K.As{\leqslant}^{O}_{(OK)_2} = RAs{\leqslant}^{O}_{(OK)_2} + KI.$$

This reaction, however, is only satisfactory in the aliphatic series. Thus, whereas ethyl arsonic acid is obtained in 70 per cent yield from ethyl iodide, the yield of arsonic acid from iodobenzene is only 8 per cent. The chief interest of the reaction lies in its providing a means of systematically alkylating arsenic (*Comptes Rendus*, cxxxvii., 925. Thus the arsonic acid (I.) can be reduced to the arsenoxide (II.) and the sodium salt of this combined with alkyl iodide to form the arsinic acid (III.). This in turn can be reduced to (IV.), which in the form of its sodium salt will combine with another molecule of alkyl iodide to form the tri-alkyl arsenoxide (V.).



Finally, the arsonic acids can be obtained by the oxidation of the arsenoxides, arsendichlorides, and arseno-compounds. The oxidation is usually best brought about

with hydrogen peroxide (*Ber.*, xli., 1514; D.R.P., 224953), but the arsenoxides can be oxidised by iodine (*Ber.*, xliii., 914) in acetic acid solution, and the arsendichlorides by chlorine :—

$$RAsCl_2 \rightarrow RAsCl_4 \rightarrow RAsO(OH)_2.$$

The oxidation of the arsenoxides by iodine is quantitative, and can be used for the estimation of these compounds.

Properties.—The arsonic acids are well crystallised compounds which, as a rule, are difficultly soluble in cold water but easily soluble in hot water. They form easily soluble salts with the alkali metals, and these salts are neutral in reaction and have the formula $ArAsO(OH)(ONa)$. The salts are best isolated by adding alcohol to their aqueous solutions. The salts with the heavy metals are insoluble, and in them, as a rule, both hydrogen atoms are replaced, *e.g.*, $ArAsO(OAg)_2$. Arsanilic acid gives a mercury salt (D.R.P. 237787) of the formula—

$$(NH_2C_6H_4As\langle{}^{=O}_{-O-}{}^{}_{OH}\rangle)_2Hg.$$

This salt is insoluble in water, but is soluble in salt solution and in glycerin.

The magnesium salts are precipitated when the arsonic acids are boiled with magnesia mixture, but are not formed in the cold (*Journ. Am. Chem. Soc.*, xxxiii., 101). This behaviour forms a convenient test for the presence of free arsenic acid in arsonic acids.

The arsonic acids when heated frequently lose a molecule of water and pass into anhydrides (*Annalen*, cci., 205) of the formula $ArAsO_2$. These anhydrides, or *arsino-compounds*, do not absorb moisture from the air, but pass back into the arsonic acid when treated with warm water.

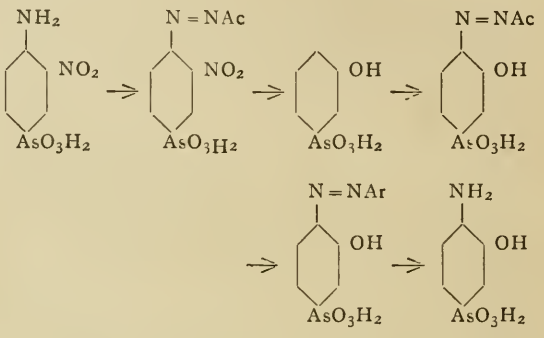
The arsonic group is, as a rule, firmly attached to the molecule, but can be replaced by halogen by treating with halogen acid. This reaction forms the standard method of determining the position of the arsonic group.

The arsonic acids are stable to oxidising agents and on reduction pass into arsenoxides, arseno-compounds, or primary arsines, according to the reducing agent used.

The *esters* (*Annalen*, cccxx., 194) have been prepared by the action of alkyl iodides on the silver salts. As a rule they are liquids, which are at once hydrolysed by water: $ArAsO(OR)_2,2H_2O = ArAsO(OH)_2,2ROH$.

The aminoaryl arsonic acids form the starting out point for the preparation of a very large number of derivatives. Thus the amino-group can be diazotised (*Ber.*, xli., 931, 3859; *Journ. Chem. Soc.*, xciii., 1893; D.R.P., 205775, 215251), and then replaced by a variety of other groups such as halogen (*Ber.*, xli., 1856), hydroxyl (*loc. cit.*, D.R.P., 223796), hydrogen, &c. (*Ber.*, xliv., 3305), in the usual way. Thus arsanilic acid can be made to yield *p*-nitriloarsonic acid, and this on hydrolysis gives the corresponding carboxy-arsonic acid. The amino-group can also be replaced by the arsonic group by means of Bart's reaction, thus rendering it possible to obtain poly-arsonic acids. The amino group can be acylated (*Ber.*, xl., 3296, xliv., 3092; D.R.P., 191548, 231969) in the usual way, and when thus protected side chains can be oxidised to carboxyl by means of alkaline permanganate (*Ber.*, xli., 931, 3859). The protected amino-compound can also be nitrated. In this case experience has shown that whereas the acetyl derivatatives are almost useless, the oxalyl derivatives and the urethanes usually give excellent results (*Ber.*, xliv., 3092; D.R.P., 231969, 232879). By this means arsanilic acid can be converted into 3-nitro-4-amino-phenyl arsonic acid, and this on reduction with sodium amalgam in methyl alcoholic solution (*Ber.*, xli., 1656; D.R.P., 206344), or with neutral sodium hydrosulphite (*Ber.*, xliv., 3092), or with ferrous chloride (*Ber.*, xliv., 3300), or with ammonium sulphide (*Ber.*, xli., 1656; D.R.P., 206344), gives the corresponding *o*-phenylene diamine arsonic acid. This gives quinoxalines when treated with α-diketones such as phenanthraquinone.

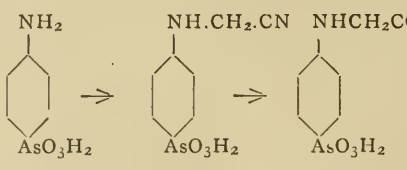
If the nitro-arsanilic acid is diazotised and the diazo compound warmed to 18° with excess of sodium acetate or other substance capable of combining with hydrochloric acid, the nitro-group is replaced by hydroxyl (D.R.P. 244166; *Ber.*, xliv., 3578); a reaction very similar to that which takes place when the diazo-salts from the corresponding nitro-sulphanilic acid are similarly treated (D.R.P. 138258). If the diazo-compound thus formed is coupled with a phenol, such as β-naphthol, and the azo-dye thus formed reduced, 3-oxy-4-amino-phenyl arsonic acid is obtained :—



More vigorous reduction of the azo-compound leads to the arseno-compound ("Salvarsan").

The presence of the nitro-group in the molecule loosens the arsonic group. Thus if the diazo-salts of nitro-arsanilic acid are boiled, the arsonic group is replaced by hydroxyl (*Ber.*, xliv., 3450, 3578). This loosening of the arsonic-group is remarkable when it is remembered that the nitro-group is present in the *meta*-position to it. The amino-group is also less firmly bound than usual as it is readily replaced by hydroxyl by the action of aqueous caustic potash (D.R.P., 235141; *Ber.*, xliv., 3449), at 80°.

The amino-group in arsanilic acid, &c. can be methylated in the usual way (*Ber.*, xli., 1514). By treatment with chloro-formic ester urethanes are obtained (D.R.P. 232879), whilst chloracetic acid leads to glycines (*Ibid.*, 204664). These glycines can also be obtained by treating the amino-arsonic acid with potassium cyanide and formaldehyde and then hydrolysing the nitrile :—

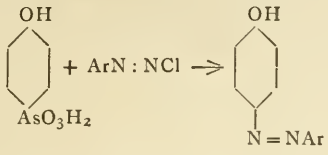


Compounds of a similar nature can, of course, be obtained by using other aldehydes, the reaction being the ordinary Bucherer and Knoevenagel process.

Unsymmetrical ureas and thioureas can be obtained (D.R.P. 213155) from the amino-arsonic acids by means of cyanates and thiocyanates, and thiol-arsonic acids have been prepared by treating the diazo-salts with xanthates and then hydrolysing the xanthic ester formed (D.R.P., 216270). Azo-dyes derived from the arsonic acids have also been described (D.R.P., 212018, 212304, 216223, 222063; *Journ. Chem. Soc.*, 1893. xciii.).

The phenolic arsonic acids can be obtained, as stated above, by fusing the phenols with arsenic acid, but the yields by this method are usually very poor. They are best obtained from the amino-compounds by boiling the diazo-salts with water (D.R.P., 205775, 215251, 223796; *Ber.*, xli., 931, 1854; lxiv., 3305, 3863). The hydroxyl group loosens the arsonic group. Thus if attempts are made to couple *p*-oxy-phenyl arsonic acid with diazo-

solutions the arsonic group is displaced (*Ber.*, xxxiv., 3449):—



Although halogens displace the arsonic group, the arsonic acids can be halogenated in non-aqueous solution, or by means of sodium hypochlorite or a mixture of potassium bromide and bromate (*Ber.*, xliii., 529). This is especially true of the amino- and phenolic arsonic acids.

The Arsinic Acids.

Formation.—These appear as side products in the preparation of arsonic acids by heating primary bases with arsenic acid (*Ber.*, xli., 2367; *Journ. Chem. Soc.*, xciii., 1180). They are more readily obtained by heating the arsonic acid with excess of primary amine, and by this means arsinic acids containing two different aryl groups can be obtained:

$$NH_2C_6H_4AsO_3H_2 + ArNH_2 = (NH_2C_6H_4)(NH_2Ar)AsOOH + H_2O.$$

The yields, however, are always very poor, and as a rule do not exceed 3 per cent. The acids are more readily obtained by Bart's reaction (D.R.P., 250264; *Pat. Anm. Kl.* 12 *o. B.*, 69659). This consists in treating a normal, or better, an *iso*-diazo salt with an arsenoxide in neutral or faintly alkaline solution, with or without the addition of copper powder or copper salts:—

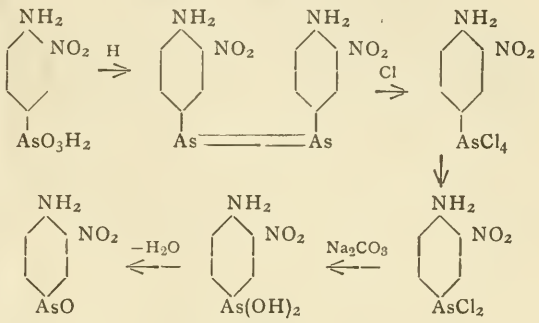
$$ArN{:}N.Ac + Ar'As(ONa)_2 = Ar.Ar'As{\leqslant}^{O}_{ONa} + NaAc + N_2.$$

Properties.—The arsinic acids form salts of the structure R_2AsOOM, where M is a monovalent metal, and also exhibit feeble basic properties. Thus diphenyl arsinic acid forms a nitrate (*Annalen*, cccxxi., 151), $Ph_2As(ONO_3)O$, when treated with a mixture of concentrated nitric and sulphuric acids, and dibenzyl arsinic acid forms a chloride, (*Annalen*, ccxxxiii., 89), $Bz_2As(OH)_2Cl$.

The arsinic acids are much less important than the arsonic acids, the best known member of the series being cacodylic acid, Me_2AsOOH. They are less soluble than the corresponding arsonic acids, give no anhydrides, and on reduction pass into the diaryl arsenoxides, $(R_2As)_2O$, of which very little is known at present.

The Arsenoxides.

Formation.—The arsenoxides can be obtained by the action of sodium carbonate on the arsendichlorides. This method is only of importance where the arsendichloride can be readily obtained. For example, it is the easiest method of obtaining *p*-dimethyl-amino-phenyl arsenoxide, as the corresponding arsendichloride is very readily formed by the action of arsenic trichloride on dimethyl aniline (*Annalen*, cclxx., 139; *Ber.*, xli., 1514). As a rule, however, the arsenoxides are best obtained by the moderated reduction of the arsonic acids (*Ber.*, xliii., 917; D.R.P., 206057, 212205, 213594, 216270, 235391, 235430). The reduction can be carried out by sulphurous acid, hydriodic acid (in which case sulphur dioxide should also be used to reduce the iodine liberated), phenyl hydrazine, thionyl chloride, or phosphorus tri-chloride. Of these hydriodic acid in the presence of sulphur dioxide gives the best results. The arsen-oxides can also be obtained by the oxidation of the arseno-compounds by means of chlorine or hydrogen dioxide. Thus Michaelis and Loesner (*Ber.*, xxvii., 267) obtained *m*-nitro-*p*-amino-phenyl arsenoxide from the corresponding arsonic acid by the following indirect method. The arsonic acid was first reduced to the corresponding arseno-compound by means of neutral sodium hydrosulphite and this then treated with chlorine. The tetra-chloride thus formed on heating with excess of the arseno-compound gave the dichloride. This on hydrolysis and loss of water gave the arsen-oxide:—



Properties.—The arsenoxides can usually be obtained crystalline, although as a class they show considerable tendency to form waxes. They are insoluble or only very slightly soluble in water, and melt at a lower temperature than the corresponding arsonic acids. They show but slight tendency to unite with water unless strongly negative groups are present in the ring, such as nitro- or carboxy-groups. They dissolve easily, however, in caustic alkalis, but only with difficulty in sodium carbonate (distinction from arsonic acids) to form salts $RAs(ONa)_2$. Esters of the type $ArAs(OR)_2$ have been isolated by Michaelis by treating the arsendichlorides with sodium alkylates (*Annalen*, cccxx., 826; cccxxi., 143). They are extremely easily hydrolysed by water.

The arsenic in the arsenoxides is less firmly attached to the molecule than is the case with the arsonic acids. Thus *p*-aminophenylarsenoxide on prolonged standing or boiling with hydrochloric acid is decomposed (*Ber.*, xliii., 923) into aniline and tri-amino-triphenyl arsine.

The oxygen of the arsenoxide group is fairly reactive. Thus when the arsenoxides are treated with sulphuretted hydrogen, sulphides are formed, *e.g.*, $ArAs = S$, and treatment with concentrated halogen acids leads to the formation of arsen dihalides. No condensation products with hydroxylamine or hydrazine have been described, but Michaelis has prepared phenyl arsenimide, $PhAs = NH$, by treating the dichloride with ammonia (*Annalen*, cccxx., 291).

As would be expected from compounds containing trivalent arsenic, the arsenoxides unite with halogen to form oxy-halides, $ArAsOCl_2$, and these on hydrolysis pass into the arsonic acids. The arsenoxides can also be oxidised to the arsonic acids by hydrogen dioxide, and by iodine in acetic acid solution (*Ber.*, xliii., 917). This latter reaction is quantitative, and can be used for titrating arsenoxides.

The arsenoxides are sufficiently powerful reducing agents to reduce Fehling's solution when boiled. On reduction with metal and acid, stannous chloride, sodium amalgam, phosphorous acid or sodium hydrosulphite in neutral solution, they pass into the arseno-compounds.

(To be continued).

Relative Electric Conductivities and Ionisation of Aqueous Solutions of Hydrochloric Acid.—J. A. Muller.—The author has determined the electric resistances of aqueous solutions of hydrochloric acid of various concentrations at 18°, 51°, and 81°, using Kohlrausch's method. From the results thus obtained he has deduced the coefficients of ionisation of solutions of the acid, and has found that ionisation diminishes rapidly as the concentration increases, but for the same concentration it varies only very slightly with the temperature.—*Bull. Soc. Chim. de France*, xi.-xii., No. 23

LOWERING OF VAPOUR PRESSURE.
(A Simple Demonstration).

By W. W. REED, M.Sc., F.I.C.

A very simple experiment illustrating the lowering of vapour pressure of a solvent by a solute at ordinary temperature is afforded by taking three similar thermometers, two of which are treated as "wet bulbs" in hygrometry, except that in one case the wick dips into the solution.

Distilled water will serve as a solvent and common salt as a solute. It will be found that the thermometer with the wick dipping into the water has a lower reading than that with wick dipping into the solution, and that both readings are lower than that indicated by dry bulb thermometer.

From these facts it can be legitimately inferred that (i.) the vapour pressures of the water and salt solution are higher than that of the aqueous vapour in the air under the conditions of the experiment, and (ii.) the vapour pressure of the water is higher than that of the salt solution, or, in other words, the vapour pressure of the pure solvent (water) is lowered by the presence of the solute (common salt).

One of many series of readings was :—

	°C.
Dry bulb	16·7
Wet bulb (salt solution)	14·4
Wet bulb (water)	13·3

When common salt is used as a solute it is found that it gradually "creeps" up the stem of the thermometer, and may attain a height of several inches.

Solutions in other solvents can be employed, *e.g.*, with organic solvents.

The following observations were made :—

	°C.	
Dry bulb	14·4	
Wet bulb (ethereal solution of aniline)	−6·6	Minimum
Wet bulb (ether)..	−8·7	temperatures.

The aniline solution was made by mixing 5 cc. of aniline with 25 cc. ordinary ether.

ON THE DENSITY OF SOLID SUBSTANCES, WITH ESPECIAL REFERENCE TO PERMANENT CHANGES PRODUCED BY HIGH PRESSURES.*

By JOHN JOHNSTON and L. H. ADAMS.

(Continued from p. 57).

Effect of Powdering a Solid upon its Density.

More than a century ago, Hassenfratz (*Gilbert's Ann.*, 1799, i., 369 ; *Ann. Chim.*, No. 27, 188) published a paper in which he claims that by breaking up a piece of glass weighing about 50 grms. into 2520 pieces (how this was accomplished without loss of material is not stated), a change in density ensued ; but his experiments are in part discordant among themselves and are by no means accurate enough to decide the point at issue. His work may therefore be left out of account entirely ; it has been mentioned here solely because its conclusions have been quoted occasionally.

The second paper, in point of time, dealing with this question, is one by G. Rose (*Pogg. Ann.*, 1848, lxxiii., 1) ; it deserves mention if for no other reason because it has been widely cited and frequently by authors who apparently have not read through the original. Rose worked, on the one hand, with gold and silver in the massive state, and with natural barite ; on the other hand, with powders produced by precipitating these substances by chemical agency ; and he found that in each case the density of the powder was the greater. He is careful to state, however, that this is no absolute proof that the density of a substance in a powdered condition is greater than that of a block of the same substance, since we cannot be sure of the complete identity of the substance in the two forms. Indeed, we now know that in very many cases the form of a substance when precipitated is different from that observed in nature or obtained by fusion. Rose's work, therefore, affords no information on the influence of the state of division of a substance on its specific gravity.

The Earl of Berkeley (*Journ. Chem. Soc.*, 1907, xci., 60) has measured carefully the densities or two sizes of fragments of natural barium sulphate. For particles remaining on a sieve, the openings of which were 0·57 mm. on a side, he finds a density which averages 4·4702, while that of particles remaining on a sieve with 0·35 mm. openings averages 4·4700. The difference between the two densities is less than 0·005 per cent—within the error of experiment. The difference between the sizes of the particles in the two cases, however, is so comparatively small that the evidence here adduced is insufficient to decide the point at issue.

It may be noted, in passing, that the above work of Rose has been cited (Cameron and Bell, *Bull.* 30, 1905, Bureau of Soils, Department of Agriculture, p. 43) in support of an observation of Spring (*Mémoires Soc. Geol. Belg.*, 1903, xvii., 13-33), according to which the amount of water required to fill the spaces of a given mass of sand is greater than would be expected if it were merely a phenomenon of occupying the air spaces. Spring's experimental work on this point is altogether insufficient to decide the question ; his conclusion is based on the *assumption* that 26 per cent of the total volume occupied by the sand consists of air spaces ; even then the difference observed was only 0·8 cc., or but 0·25 per cent of the total volume of the sand. In what follows it will be shown directly that this conclusion is false, since the density of solid substances, determined by the pyknometer, is found to be independent of the size of the particles, so long as these are strictly homogeneous, or even to show a slight decrease as the size of particle decreases; whereas, according to Spring's conclusion, the density should increase as the size of the particles decreases. A number of other early papers are cited by Spring in his first paper (*Bull. Acad. Roy. Belg.*, 1883, [3], vi., 507) dealing with the change of densities of solids ; these are all, however, concerned with changes of density produced by crystallisation, vitrification, by tempering, hammering, or annealing, and will be considered later.

Our experiments were made with quartz and potassium sulphate. The material was passed through a series of sieves, rated as 40, 60, 80, 100, 120, 150, and 200 meshes to the linear inch ; the various samples were collected and dried at 200° for half an hour (special experiments showed that the density of even the finest material was not appreciably affected by exposure to the air for 48 hours). The earlier determinations of densities were made with the old style of pyknometer ; the later ones with the new style described above. The liquids used were water and xylene (for which $d_4/_{30} = 0{\cdot}85262$), the latter being used exclusively with the salts.

Table II.—$d_4/_{30}$ *of* K_2SO_4 *Particles of Various Sizes.*

Old Style Pyknometer.	$d_4/_{30}$.
Between 40 and 60 mesh.. ..	2·6574
	2·6574
Between 100 and 120 mesh ..	2·6563
Finer than 200 mesh..	2·6563

The results with potassium sulphate are brought together in Table II., which shows that the difference in density between the fine and the coarse powder is here scarcely greater than the error of experiment. A microscopical examination of the potassium sulphate showed that the crystals were free from inclusions or inhomogeneities of any kind.

* From the *Journal of he American Chemical Society*, xxxiv., No. 5.

For quartz the results shown in Table III. were obtained. In this table each value of density represents a determination on a separate sample of material. It will be noted that with increasing fineness, the density increases by a small but definite amount, reaching a maximum with particles 0·05 mm. in diameter (200 A) and then decreasing in the case of the very finest material (200 B).

This seemed difficult to account for until we discovered that, although a previous microscopical examination of one lot of ground quartz indicated that it was quite homogenous, nevertheless the coarser particles of the lot from which our samples were taken contained a number of minute gaseous and solid inclusions; the finer particles (200 A), however, were almost entirely free from such inclusions. This fact accounts for the greater density of the 200 A. It is of interest to note in this connection that H. E. Merwin (*loc. cit.*) found the density of a number of fragments of clear quartz from different localities to be 2·6495 at 20°. Correcting the density to 25° (see *Smithsonian Physical Tables*, 1904, 215-216) it becomes 2·6490—almost identical with the density of the 200 A material. This shows with great certainty that there is no difference in density between fragments of quartz 1 cm. in diameter and particles 0·05 mm. in diameter.

Table III.—$d_{4}/_{25}$ *of Quartz Particles of Various Sizes.*

Old Style Pyknometer.

	Between 40 and 60 mesh.	Between 100 and 120 mesh.	Finer than 200 mesh.
	2·6487	2·6466	2·6492
	2·6455	—	2·6481
	2·6456	—	2·6468
	2·6471	—	2·6471
	2·6466	—	2·6485
	2·6472	—	2·6495
	—	—	2·6483
	—	—	2·6463
Average ..	2·6468	2·6466	2·6480

New Style Pyknometer.

Between 40 and 60 mesh.	Between 80 and 100 mesh.	Finer than 200 mesh.	200 A(*a*)	20 B(*a*)
2·6471	2·6478	2·6488	2·6492	2·6483
2·6469	2·6476	2·6477	2·6486	2·6477
—	—	2·6483	—	—
—	—	2·6481	—	—
2·6470	2·6477	2·6482	2·6489	2·6480

(*a*) A quantity of the powdered quartz which passed through a 200-mesh sieve was separated by a process of sedimentation into two nearly equal fractions. The coarser fraction (200 A), as seen under the microscope, consisted of sharp grains very uniform in size, namely about 0·05 mm. across. The finer material (200 B) was composed of particles, the size of which ranged from 0·02 mm. on down to the limit of vision of the microscope and probably beyond it.

With potassium chloride, the crystals of which contain a considerable number of holes, the density of the fine powder is considerably higher than that of the coarse material, as the following results indicate:—

Table IV.—$_{4}/_{30}$ *of* KCl *Particles of Various Sizes.*

Old Style Pyknometer.

	With sifted samples.	With ground and sifted samples.
Between 20 and 40 mesh	1·9786	—
Between 80 and 100 mesh ..	1·9829	—
Between 100 and 120 mesh ..	1·9837	19818
Between 150 and 200 mesh ..	1·9841	19828

It may be remarked that the density of the finest product was the same independently of whether it had been obtained by simply separating the fine crystals originally present or by grinding up some of the materia of size between 20 and 40 mesh and subsequently sizing it between the 150- and 200-mesh sieves. These experiments suffice to show that when homogeneous material, free from cracks or holes, is powdered, the change of density thereby produced is but little greater than the error of the method employed. It may be noted, however, that the change, if real, is in both cases a decrease; and this may be a manifestation of the same phenomenon which is observed when metals are strained (cf. *postea*).

(To be continued)

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, January 23rd, 1913.

Sir Archibald Geikie, K.C.B., President, in the Chair.

Papers were read as follows:—

"*Metabolism of Lactating Women.*" By Edward Mellanby.

"*Colour Adaptation.*" By F. W. Edridge-Green, M.D., F.R.C.S.

As in dark adaptation there is a considerable effect which takes place immediately on entering a dark room, so is there a considerable effect produced when a person enters a room illuminated by an artificial light, having previously been in daylight. This effect, which may be designated colour adaptation, increases with the time during which the eyes are subjected to the adapting light. The effect of colour adaptation was estimated by four methods.

The following is a summary of the results:—

1. In colour adaptation the retino-cerebral apparatus appears to become less and less sensitive to the colour corresponding to the dominant wave-length, and to set up a new system of differentiation.

2. When light of a composition differing from that of daylight is employed to illuminate objects, an immediate and unconscious estimation of the colours of these objects is made in relation to this light, the light employed being considered as white light.

3. No colour is seen of which the physical basis is not present in the light employed.

4. When spectral regions are examined with a colour-adapted eye, that of the dominant wave-length appears colourless, whilst those immediately on either side of it appear to be shifted higher and lower in the scale respectively.

5. There is an immediate colour adaptation as well as a colour adaptation after longer stimulation with the adapting light.

6. Colours which correspond to the dominant wave-length of an artificial light are with difficulty discriminated from white by this light.

7. Colour adaptation may bring two colours below the threshold of discrimination, so that the two appear exactly alike, although by another kind of light a difference is plainly visible.

8. Colour adaptation increases the perception of relative difference for colours other than the dominant.

9. The conscious judgment has very little effect in colour adaptation.

10. Colour adaptation greatly helps in the correct discrimination of colours and masks the effects of the very great physical differences which are found in different kinds of illumination.

11. Spectral yellow, after colour adaptation to green, still appears yellow and not red.

12. Colour adaptation appears to produce its effect of subtraction by the dominant colour sensation, and not by directly increasing the complementary. Spectral blue does not appear brighter after colour adaptation to yellow.

"*Trichromic Vision and Anomalous Trichromatism.*" By F. W. EDRIDGE-GREEN, M.D., F.R.C.S.

The following are the conclusions arrived at after the examination of a large number of persons belonging to each class:—

1. Trichromic vision (on the author's classification of colour-vision) is not synonymous with anomalous trichromatism.

2. Many persons with otherwise normal colour perception make an anomalous equation.

3. Many colour-blind persons (dichromics and trichromics) make an absolutely normal match with no greater mean deviation than the normal.

4. Colour weakness is not characteristic of anomalous trichromatism but of trichromic vision.

5. Anomalous trichromatism and colour weakness are not synonymous.

6. A large mean deviation indicates colour weakness.

7. Anomalous trichromatism appears to be due to an alteration in the normal relations of the response to the three colours (lights) used in the equation. If the eye be more or less sensitive to one of the components of the mixed colour whilst the other has its normal effect, an anomalous equation will result. An anomalous equation will also result when the yellow is more allied to green or red than is normal.

"*Transmission of Environmental Effects from Parent to Offspring in* Simocephalus vetulus." By W. E. AGAR, Glasgow University.

"*Relation of the Islets of Langerhans to the Pancreatic Acini under Various Conditions of Secretory Activity.*" By JOHN HOMANS, M.D.

"*Contributions to the Histo-chemistry of Nerve; on the Nature of Wallerian Degeneration.*" By H. O. FEISS and W. CRAMER.

"*On Onychaster, a Carboniferous Brittlestar.*" By I. B. J. SOLLAS.

"*Herbage Studies.* II. *Variation in* Lotus corniculatus *and* Trifolium repens (*Cyanophoric Plants*). By Prof. H. E. ARMSTRONG, F.R.S., E. F. ARMSTRONG, and E. HORTON.

During the past summer, by testing very carefully the apparently acyanophoric form of *L. corniculatus* described in Part I., it has been found that this contains a minute proportion of cyanide; moreover, two varieties of this form have been met with, in close proximity, the one rich in enzyme, the other having little, if any, enzymic activity towards linamarin. The manner in which the plant has been found to vary, especially in different parts of Scotland, is discussed at some length.

Attention has also been directed to white clover in particular, on account of its importance as the chief leguminous plant in pasture lands. The authors have been forestalled by Mirande (*Comptes Rendus*, 1912, vol. clv., p. 651) in the discovery that this plant is cyanophoric, like *L. corniculatus*. But their observations go further and show that whilst the wild form of *Trifolium repens* is uniformly more or less cyanophoric, the cultivated form is destitute of cyanide.

Both forms are moderately active towards the glucosides linamarin, prunasin, and salacin, resembling *L. corniculatus* in this respect; and striking differences in the enzymic activity of the wild form have been met with corresponding to those in the latter plant. In view of the very different values which various pastures are known to have as fattening lands, it is hoped that it may be possible, during the coming season, to institute systematic feeding trials with the two forms of white clover, to ascertain whether the chemical differences that have been discovered can in any way be correlated with differences in their value as animal foods.

"*Phenomena of 'Narcosis Progression' in Mammals.*" By T. G. BROWN.

"*Reciprocal Innervation and Symmetrical Muscles.*" By Prof. C. S. SHERRINGTON, F.R.S.

"*On the Manganese Content of Transplanted Tumours.*" By F. MEDIGRECEANU, M.D.

"*Preliminary Note on a New Bacterial Disease of* Pisum sativum." By DOROTHY M. CAYLEY.

"*Non-identity of* Trypanosoma brucei (*Plimmer and Bradford*, 1899) *with the Trypanosome of the same Name from the Uganda Ox.*" By J. W. W. STEPHENS, M.D., and B. BLACKLOCK, M.D.

CHEMICAL SOCIETY.

Ordinary Meeting, January 23rd, 1913.

Prof. PERCY F. FRANKLAND, LL.D., F.R.S., President, in the Chair.

MESSRS. James W. McBain, M. Nierenstein, Arthur J. Hale, and W. Compton Till were formally admitted Fellows of the Society.

The PRESIDENT referred to the loss sustained by the Society through death, of—

Arthur Crozier Claudet (elected June 18th, 1902, died January 17th, 1913); John McArthur (elected December 1st, 1887, died December 9th, 1912); Arthur Richardson, elected June 18th, 1885, died June 1st, 1912); Henry Seward, elected January 20th, 1870, died April 12th, 1912).

Certificates were read for the first time in favour of Messrs. William Beath, 152, St. George's Road, Hull; Percy Charles Burr, B.Sc., Essex Lodge, Ravensbourne Park, Catford, S.E.; Harold Reginald Septimus Clotworthy, B.A., B.Sc., 39, Trinity College, Dublin; John Albert Cockshutt, M.Sc., Queen's College, Taunton; Tin Kari Ghose, B.A., 23/1, Baniatola Street, Hatkhola P.O., Calcutta; George Watson Gray, 8, Inner Temple, Liverpool; Daniel William Lloyd, B.Sc., The Manse, Ormonde Road, Kilkenny; Walter Cyril Loynes, Eastfield, Comberton-road, Kidderminster; Alexander Killen Macbeth, M.A., B.Sc., 3, Victoria Terrace, Cregagh, Belfast; Henry Stephen Martin, 64, Dyke Road, Brighton; Aylmer Henry Maude, Great Baddow, Chelmsford; Joseph Horsnell May, 21, Donovan Avenue, Muswell Hill, N.; Ernest Joseph Mumford, 67, Hatherley Road, Walthamstow, N.E.; John Walter Smith, B.Sc., 48A, Hurstbourne Road, Forest Hill, S.E.; Hubert Rogers Wood, care of Messrs. Fenner, Alder and Co., Ltd., Millwall, E.

A Certificate has been authorised by the Council for presentation to ballot under Bye-law I. (3) in favour of Mr. Jonathan Parker, care of The Wattle Extract Co., 42, Anglo-African House, Durban, Natal.

Of the following papers, those marked * were read:—

*1. "*The Constituents of the Rhizome and Roots of Caulophyllum Thalictroides.*" By FREDERICK BELDING POWER and ARTHUR HENRY SALWAY.

The material employed for this investigation consisted of the rhizome and roots of the American plant, *Caulophyllum thalictroides* (Linné), Michaux (Nat. Ord. *Berberidaceae*).

A preliminary test showed the presence of an alkaloid, and a small amount of an enzyme was obtained, which slowly hydrolysed amygdalin.

An alcoholic extract of the ground material, when distilled in a current of steam, yielded a small amount of an essential oil. From the alcoholic extract the following definite compounds were isolated: (i) Methylcytisine, $C_{12}H_{16}ON_2$ (m. p. 137°; $[\alpha]_D$ −221·6°), the *picrate* of

which melts at 228°; (ii) a crystalline glucoside, *caulosaponin*, $C_{54}H_{88}O_{17},4H_2O$ (m. p. 250—255°), which on hydrolysis is resolved into *caulosapogenin*, $C_{42}H_{66}O_6$ (m. p. 315°), and dextrose; (iii) a new crystalline glucoside, *caulophyllosaponin*, $C_{66}H_{104}O_{17}$ (m. p. 250–260°; $[\alpha]_D$ +32·3°), which on hydrolysis is resolved into *caulophyllosapogenin*, $C_{56}H_{88}O_9$ (m. p. 315°), and arabinose; (iv) a phytosterol, $C_{27}H_{46}O$ (m. p. 153°); (v) citrullol, $C_{28}H_{45}O_2(OH)_3$; (vi) a mixture of fatty acids, consisting of palmitic, stearic, cerotic, oleic, and linolic acids. The alcoholic extract also contained a quantity of sugar, which yielded *d*-phenylglucosazone (m. p. 210°), and a comparatively small amount of resinous material.

Methylcytisine represents the alkaloid first isolated by J. U. Lloyd (*Proc. Amer. Pharm Assoc.*, 1893, xli., 115), and designated by him "caulophylline," but its composition had not heretofore been known. The glucoside to which the name of *caulosaponin* has now been given is undoubtedly identical with a glucosidic substance, which was likewise first obtained by Lloyd, and termed "leontin," although its formula had not been correctly determined. Its complete characterisation has now been effected.

*2. "*Ionisation and the Law of Mass Action.*" By WILLIAM ROBERT BOUSFIELD.

The author showed that the dilution laws for strong electrolytes formulated by Rudolphi, van't Hoff, and Kohlrausch (with some others) are all true in the region of very high dilution, all being equivalent in that region to the simple law: $(1-\alpha)=h-\frac{1}{2}\times$Constant, where h is the total number of molecules of water per mol. of solute. In this region the law for weak electrolytes becomes: $(1-\alpha)=h-1\times$Constant.

The fundamental difference between weak and strong electrolytes may therefore be thus stated:

For weak electrolytes, at great dilution, the active mass of the undissociated fraction is inversely proportional to the mass of the water.

For strong electrolytes, at great dilution, the active mass of the undissociated fraction is inversely proportional to the square root of the mass of the water.

The question of the best method of arriving at the true coefficient of ionisation was also considered.

DISCUSSION.

In reply to Dr. Senter, Mr. BOUSFIELD stated that he thought it was by a special consideration of the active mass of the dissociated fraction of the solute that the formulæ would be ultimately brought into conformity with the law of mass action. As to the manner in which the theory of ionic sizes reconciled the series of values for freezing-point depressions, he referred to a former paper (*Phil. Trans.*, 1906, A, ccvi., 149).

*3. "*The Character and Cause of the Blue Fluorescence which Develops in Alkaline Solutions containing Quinol Sulphite on Exposure to the Air.*" By THOMAS CUNNINGHAM PORTER.

Moist *p*-benzoquinone each react directly with neutral as well as with acid alkali-metal sulphites to form compounds which differ according to which of the reagents is in excess.

With excess of sulphite remarkably stable compounds such as $(NH_4HSO_3)_2C_6H_4O_2$ are produced. These, in turn, form with alkali- and alkaline-earth-metal hydroxides substances which give brilliantly fluorescent aqueous solutions.

The character of this blue fluorescence was described, and it was shown that the fluorescence of "stale" quinol and sulphite photographic developers is identical with it, and due to the same cause.

*4. "*The Form of Extinction Curves; Cobalt Nitrate Solutions.*" By THOMAS RALPH MERTON.

An investigation has been made of the extinction curves of cobalt nitrate solutions, which exhibit a single absorption band in the visible spectrum. It has been found that the curve may be represented within the limits of experimental error by a simple mathematical expression. It is suggested that many of the apparently anomalous forms of extinction curves which are found are due to the superposition of some such simple type as the above.

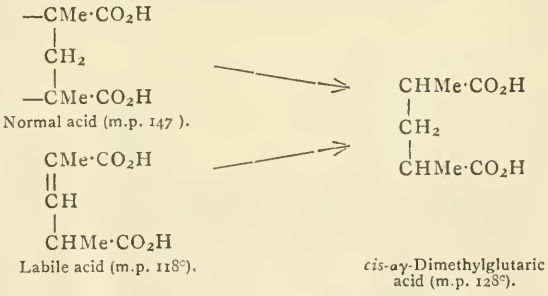
5. "*The Hydrolysis of Ethylene Glycol Diacetate.*" (Preliminary Note.) By ERNEST GRAHAM BAINBRIDGE.

The author has investigated the action of sodium ethoxide in alcoholic solution on ethylene glycol diacetate at the boiling point of the mixture, and finds that ethyl acetate is produced. A yield of 85 per cent of ethylene glycol can readily be obtained as follows: A molecular mixture of ethylene glycol diacetate and sodium ethoxide is heated on a steam-bath to remove the ethyl acetate and excess of alcohol, the residue treated with water, and distilled under diminished pressure. The distillate is then fractionated, the yield being almost that required by theory.

The author is at present engaged in working out the mechanism of the reaction, and in further investigating the action of sodium ethoxide and sodium hydroxide on ethylene glycol diacetate.

6. "*The Chemistry of the Glutaconic Acids.* Part VII. *The Normal and Labile Forms of αγ-Dimethylglutaconic Acid and their Reduction to cis-αγ-Dimethylglutaric Acid.*" By JOCELYN FIELD THORPE and ARTHUR SAMUEL WOOD.

It has been found possible to isolate the labile modification of αγ-dimethylglutaconic acid, which is a crystalline substance melting at 118°. The view expressed in previous parts of this series that both the labile and normal forms of substituted glutaconic acids have a *cis*-configuration is supported by the fact that both the labile and normal forms of αγ-dimethylglutaconic acid yield *cis* αγ-dimethylglutaric acid on reduction:



The properties of the labile acid were described.

7. "*The Influence of Water on the Partial Pressure of Hydrogen Chloride above its Alcoholic Solutions.*" By WILLIAM JACOB JONES, ARTHUR LAPWORTH, and HERBERT MUSCHAMP LINGFORD.

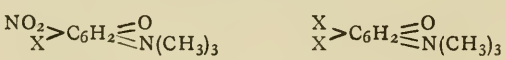
The authors have determined the partial pressures of hydrogen chloride above its anhydrous alcoholic solution over a range from 0·275N to 3·19N, and also in presence of small quantities of water up to 2·5 grm.-molecules per litre. The apparatus used consisted of three saturators of the type devised by Gahl, united by ground-glass joints with mercury seals, and containing in order, anhydrous ethyl alcohol, the hydrogen chloride solution, and water respectively. Hydrogen was passed through the apparatus, which was wholly immersed in a thermostat at 25° ± 0·05, the use of air having been found to lead to chemical change and inconsistent results; the volume of gas used was determined from the weight of alcohol which passed from the first saturator, whilst the hydrogen chloride expelled from the second solution (which remained practically constant in concentration) was ascertained by titration of the liquid in the third saturator.

The results obtained were consistent, and the method appeared to give satisfactory values, except possibly with very low pressures (0·2 mm. or less), when water was present.

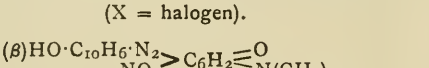
A somewhat complicated formula, based on Dolezalek's expression, serves to express the influence of the concentration of hydrogen chloride or water, or both together, over a wide range.

8. "*Quinone-ammonium Derivatives.* Part II. *Nitrohaloid, Dihaloid, and Azo-derivatives.*" By RAPHAEL MELDOLA and WILLIAM FRANCIS HOLLELY.

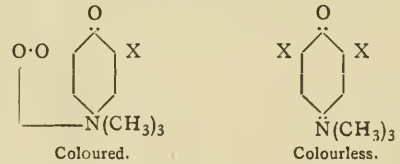
In continuation of their former paper (*Trans.*, 1912, ci., 912) the authors described new types of quinone-ammonium derivatives containing halogens and azo-groups. The isolation of these compounds had been made possible by the discovery that the nitro-groups in the dinitrotrimethylammonium-benzoquinone described in their last communication could be either partly or completely reduced, the resulting amino- and diamino-compounds being amenable to treatment by all the ordinary diazo-methods. The compounds described were of the types :—



(X = halogen).



The preparation of the bisazo-compound from β-naphthol and the isolation of the first of the quinone-ammonium derivatives containing an asymmetric nitrogen atom was preliminarily indicated by the authors. The relationship between the colour and constitution of the compounds was further considered, and preference provisionally given to the "aci"-form for the nitro-group in the nitro-derivatives which are invariably coloured, the corresponding haloid derivatives being colourless :—



Coloured. Colourless.

The "quinole" structure for the hydrated form (*Trans.*, 1912, ci., 918) was considered to have received further support from the experimental results obtained.

9. "*The Chemical Nature of some Radioactive Disintegration Products.*" By ALEXANDER FLECK.

It has been found that uranium-X, mesothorium-2, radioactinium, thorium-B and C, actinium-B and C, radium-B, C, and E, have chemical properties identical with those of some already known element. Uranium-X and radioactinium are chemically similar to and non-separable from thorium, mesothorium-2 is non-separable from actinium, thorium-B is non-separable from lead, radium-B and actinium-B are extremely similar to lead and most probably non-separable from it; thorium-C, radium-C, and actinium-C are very closely allied to bismuth, and probably chemically similar to it. The present view that there is only one product, radium-E, between radio-lead and polonium has been confirmed by the direct measurement of the growth of radium-F from radium-E. Radium-E has chemical properties identical in all respects with those of bismuth.

10. "*Action of Ammonia and Alkylamines on Reducing Sugars*" By JAMES COLQUHOUN IRVINE, ROBERT FRASER THOMSON, and CHARLES SCOTT GARRETT.

The action of ammonia, in methyl-alcoholic solution, on various sugar derivatives has been re-investigated. The reactions were carried out in the cold, and in the absence of a catalyst. From the fact that sucrose, α-methylglucoside, and tetramethyl α-methylglucoside were unaffected under these conditions whilst gluconolactone was converted into *gluconamide*, the deduction is made that the formation of the so-called "imines" of the sugars is due to condensation of the reducing group with one molecule of ammonia.

These imines are thus to be regarded as unstable amino-sugars, and the absence of salt formation is due to the ready hydrolysis of the complexes. According to this view of the structure of these compounds, reducing sugars should be capable of condensation with both primary and secondary amines, and it is now shown that glucose reacts with ethylamine, diethylamine, and dimethylamine to give *ethylaminoglucose*, *diethylaminoglucose*, and *dimethylaminoglucose* respectively. Ethylaminoglucose is crystalline, and shows measurable mutarotation, and the same change was detected in the case of "glucoseimine."

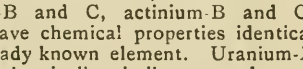
The action of ammonia on lævulose gave, in addition to 2 : 5 - ditetrahydroxybutylpyrazine, a second product, $C_6H_9O_4N$, which, although inactive, was converted into glucosephenylosazone, displaying the normal rotation. The constitution of this product, and the possible cause of the great variation in stability shown by amino-sugars were discussed.

11. "*The Chlorination of Iodophenols.* Part II. *The Chlorination of* o-*Haloid Derivatives of* p-*Iodophenol.*" By GEORGE KING and HAMILTON MCCOMBIE.

The work described by Brazier and McCombie (*Trans.*, 1912, ci., 968) on the chlorination of *p*-iodophenol has now been extended to other *p*-iodophenols in which one or both of positions 2 and 6 is occupied by another halogen atom.

Willgerodt (*Ber.*, 1892, xxv., 3495) states that when 2 : 4 : 6-tri-iodophenol is chlorinated in chloroform solution only an oily substance results. The authors have confirmed this result, but were able to obtain an iodo-dichloride when either carbon tetrachloride or light petroleum was employed as the solvent. This iodo-dichloride is more stable than the one derived from *p* iodophenol, and differs further from the latter compound in that on decomposition chlorine is liberated and tri-iodophenol is regenerated.

As both the solvent and the temperature employed in these chlorinations had an influence on the products obtained, a detailed study of these influences was made. In glacial acetic acid at 15° the main products of the reaction were (1) a tetrachloro-compound—



and (2) chloroanil. In boiling acetic acid solution a copious yield of chloroanil was obtained.

2 : 6 - Dibromo-4-iodophenol gave an iodo-dichloride which resembled the compound derived from tri-iodophenol in that on decomposing chlorine is evolved and the original phenol is regenerated. It has been shown by Brazier and McCombie that 2 : 6-dichloro-4 iodophenol can be converted into an iodo-dichloride which decomposes with evolution of hydrogen chloride and the formation of a further substitution product. Hence the presence of two bromine or two iodine atoms in positions 2 and 6 protects the hydrogen atoms 3 and 5 from attack.

2 : 4-Di-iodophenol and 2-bromo 4 iodophenol both yield iodo-dichlorides which on decomposing lose hydrogen chloride, and give 6-chloro-2 : 4-di-iodophenol and 6-chloro-2-bromo-4-iodophenol respectively.

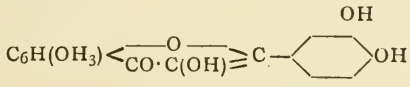
While the iodophenols described yield unstable iodo-dichlorides, it has been found in this case, as was noticed in the case of *p*-iodophenol, that the acyl derivatives yield stable iodo-dichlorides.

In the case of all the polyiodo-compounds which are described it was found that only one of the iodine atoms becomes tervalent. In these cases evidently the hydroxyl and acyl groups destroy the tervalency of the iodine atoms in the same way as the methyl group does in 2 : 4-di-iodotoluene (Willgerodt and Simonis, *Ber.*, 1906, xxxix., 269), and the nitro-group in 3 : 5 - di-iodonitrobenzene (Willgerodt and Ernst, *Ber.*, 1901, xxxiv., 3406).

12. "*Quercetagetin.*" By ARTHUR GEORGE PERKIN.

Quercetagetin, $C_{15}H_{10}O_8$, the colouring matter of the African marigold, *Tagetes patula* (*Proc.*, 1902, xviii., 75),

when methylated with excess of methyl iodide and alkali gives *quercetagetin pentamethyl ether*, $C_{15}H_5O_3(OMe)_5$, pale yellow needles, m. p. 161–162°, and *quercetagetin hexamethyl ether*, $C_{15}H_4O_2(OMe)_3$, colourless needles, m. p. 157—158°. *Quercetagetin hexaethyl ether*, $C_{15}H_4O_2(OEt)_6$, colourless needles, m. p. 139—141°, by hydrolysis with alcoholic potassium hydroxide gives protocatechuic acid diethyl ether, and a ketone, *quercetagetol tetraethyl ether*, $HO{\cdot}C_6H(OEt)_3{\cdot}CO{\cdot}CH_2{\cdot}OEt$, prismatic needles, m. p. 46—48°, which yields the *oxime*, $C_{16}H_{25}O_6N$, m. p. 93—95°, and with permanganate an acid (*quercetagetinic acid*), needles, m.p. 100–102°. The pentahydroxyflavonol constitution—



is assigned to quercetagetin, which is thus isomeric with myricetin (*Trans.*, 1911, xcix., 1721), but the positions of the hydroxyl groups, O:OH:OH:OH·, in the tetrahydroxybenzene nucleus have not yet been decided. Acetylquercetagin melts at 209—211°, and not at 203—205° as previously stated.

(To be continued).

PHYSICAL SOCIETY.

Ordinary Meeting, January 24th, 1913.

Prof. C. H. Lees, F.R.S., Vice-President, in the Chair.

A paper entitled "*The Resistance of Electrolytes*," by Messrs. S. W. J. Smith and H. Moss, was read by the former.

Some experiments upon this question were exhibited before the Society in 1911. In these a modification of Wien's method was used—the optical telephone being replaced by a vibration galvanometer—and the conclusion was drawn from them that the resistance of an electrolyte varies to an easily perceptible degree with the frequency of the alternating currents to which it is subjected.

The authors point out that the terminal difference of potential and the current in a branch of a network containing capacity and self-induction may be in the same phase although their ratio does not give the resistance of that branch. This will happen (whether the branch contains an electrolyte or not) if there is leakage through the condensers, causing the P.D.'s between their plates to be out of quadrature with the current. The apparent resistance of the branch will then be a function of the frequency of the alternating currents circulating in the bridge, and Wien's method (as Wien himself points out) will give this apparent resistance only.

It is therefore unsound to use the method to test whether the resistivity of an electrolyte depends upon the frequency of the currents to which it is subjected, unless it is shown that the effects of leakage through the electrolytic condensers can be neglected or allowed for.

A particular case was indicated by the authors, in which the leakage could be made large or small at will. The results for this case had been interpreted by Krüger, without assuming any variation of resistance with frequency, in a manner which seemed satisfactory to them.

In order, however, to remove or justify any doubt upon the question they have performed test experiments by a simple and direct method which was described. It depends upon simultaneous measurement of the voltage between the ends of a tube containing the electrolyte and of the current passing through it. The former was measured by means of an Ayrton-Mather electrostatic voltmeter connected to auxiliary electrodes and the latter by means of a Duddell thermo-galvanometer.

In the cases examined it was found that the resistivity of the electrolyte was constant within 0·05 per cent, whether steady currents or currents of any frequency up to 2300 alternations per second were used.

Until the instruments were calibrated by means of a metallic resistance there appeared to be a small difference of about 1 part in 600 between the resistance as measured by continuous currents and the values obtained with alternating currents.

Some supplementary experiments were made with the object of elucidating the peculiar behaviour of the instruments which this calibration disclosed. On account of the smallness of the effect its cause could not be completely ascertained; but the fact that the apparent contact P.D. within the voltmeter was a function of the applied voltage, decreasing as the latter was raised, would cause an effect of the same sign as that observed. Unallowed-for leakage, greater with steady than with alternating currents, might also provide a partial explanation of the results.

Mr. A. Campbell expressed himself interested, and thought that the very small discrepancy described might be due to the method employed, which involved taking direct readings of both volts and ampères. He had not noticed the effect himself. It might be that it only occurred in particular instruments. He thought the effect was more likely to lie in the thermo-ammeter than in the electrostatic voltmeter.

Mr. F. E. Smith asked how long the current was left on before readings were taken, and was it possible that with direct currents the effect might be due to differences of concentration round the electrodes. He agreed, however, that the fact that gold showed the same phenomena seemed to negative this possibility.

Mr. R. S. Whipple suggested a radio-active leak in the voltmeter.

Prof. G. W. O. Howe thought the discrepancy was too regular to be due to any radio-active leaks.

Dr. H. F. Haworth remarked that Dr. Smith in his equations had assumed R to be independent of the frequency. He suggested that the resistance decreased as the frequency was raised because the complex molecules in the solution were shaken asunder, and also suggested that using platinised electrodes instead of ordinary platinum might have the effect of disintegrating these complex molecules in the solution, thereby giving a constant value of the resistance. The mercury electrodes employed by Dr. Smith might also have just the same effect. Heating the solution also decreases the resistance by breaking up the complex molecules.

Mr. G. D. West asked if the authors had used lower frequencies than 100.

Mr. G. L. Addenbrooke remarked that it had been known to him for a long time that contact P.D. was by no means constant. It could be altered by fingering the apparatus. He thought the deflections with alternating currents might be influenced by vibration of the electrometer needle.

Mr. F. P. Worley remarked that physical chemists were entirely dependent on physicists for the method they employed in measuring electrolytic resistances, and any suggestions for improving methods followed by chemists would be very acceptable to them.

Prof. C. H. Lees remarked that Dr. Smith had given a very simple explanation of the facts, and it was open to Dr. Haworth to explain them in any other way if he preferred.

The Authors replied briefly to the various questions asked and criticisms offered.

A paper on "*The Electrical Conductivity and Fluidity of Strong Solutions*" was read by Mr. W. S. Tucker.

In adopting Callendar's association theory of strong solutions (*Proc. Roy. Soc.*, A, lxxx., 466) some difficulty is experienced in getting the strongest solutions of electrolytes to conform to the laws laid down. This is attributed to the inaccuracy of the ionisation data, which are derived from observations on electrical conductivity. It may be supposed that the viscosity of the solution will affect its conductivity, and the author carried out a series of

experiments to determine if there were any definite relation between conductivity and fluidity in the case of calcium chloride solutions.

The feature of these determinations is the simultaneous observation of viscosity, electrolytic resistance, and temperature.

Solutions were contained in an unsilvered Dewar cylinder, which permitted a slight adjustment of temperature if necessary.

A platinum thermometer records the temperature, and is caused to oscillate in the solution by a stirring mechanism.

In so doing it draws a platinum scoop through the liquid and thus acts as an efficient stirrer. The conductivity cell and the viscometer were bound to the thermometer by rubber bands. While the thermometer oscillates the readings of electrical resistance were measured by means of the rotating commutator and bridge. The viscometer was in the form of a capillary pipette, which was immersed in the solution a known depth. The levels of the inflowing liquid were indicated electrically, and hence the rates of inflow could be accurately estimated and compared with that of water. Viscosities correct to less than 1 per cent were obtained.

Isothermal Observations.—Perfectly smooth curves for conductivity and fluidity were obtained, even when the super cooled melted crystals were included. No definite connection between conductivity, fluidity, and concentration can be derived if the latter is expressed in terms of volume, but if concentration is expressed as a ratio of masses—molecules of solute to 100 molecules of solvent—the ratio conductivity C/fluidity F stands in linear relation to the concentration n when the latter exceeds one-fourth its maximum value. In spite of the enormous variations of the quantities in this ratio C/nF has values differing at most only 2 per cent from the mean.

Examination of similar results by Bousfield and Lowry for sodium hydrate give striking agreement with this conclusion. However, owing to the dependence of C and F on linear dimensions, this relation is difficult to interpret.

Variations with Temperature.—One solution of nearly cryohydric strength was examined at temperatures from 40° C. to −50° C. The same tube and apparatus were employed, and for lower temperatures liquid air was used as a cooling agent. The failure of the fluidity-temperature and conductivity-temperature curves to exhibit the same variations was clearly shown.

Conductivities of various solutions were examined from 40° C. to their freezing-points and the curves C/n and temperature plotted. The increasing curvature with concentration is shown, and the error involved in applying the ratio, molecular conductivity to that at infinite dilution, obtained at one temperature, to indicate ionisation at another temperature, is quite apparent.

Moreover, within the limits of accuracy employed no indication is given of the existence of different hydrates.

The results obtained above suggest that no reliance can be placed on ionisation data derived from electrical conductivity observations.

Prof. C. H. LEES remarked that the observations should be extended to see whether other strong solutions gave a simple relation between the fluidity and the resistance.

Mr. F. P. WORLEY thought the ratio of the conductivity to the concentration when the latter was expressed as so many grm.-molecules of salt per 100 of water had a rather doubtful meaning.

Mr. F. E. SMITH asked if Mr. Tucker had got any explanation of the fact that he found the cryohydric-point 2½° higher than previously found.

The AUTHOR, in reply, stated that Morse and Fraser, working on the osmotic pressure of sugar solutions, found it bore a simple relation to the concentration per 100 molecules of water and not to the volume concentration. In reply to Mr. F. E. Smith, Roozeboom had used an alcohol thermometer in determining the cryohydric-point. He might also have got it too low, due to uper-cooling.

INSTITUTE OF CHEMISTRY.

THE second of two lectures on "Chemistry in Gas Works" was delivered by Mr. W. J. A. BUTTERFIELD, M.A., F.I.C., on January 31st, 1913, in the Chemical Lecture Theatre of University College (by kind permission of the Committee of the College). Prof. Raphael Meldola, D.Sc., LL.D., F.R.S., President of the Institute, was in the Chair.

The first of the two lectures had been delivered on December 18th last, and dealt chiefly with the requirements of a public gas supply, the magnitude of operations in the gas industry, and the manufacture of gas by the carbonisation of coal and by the carburetted water gas process. In his second lecture Mr. Butterfield first referred to the principles underlying the condensation of crude gas and the extraction of tar from it. The conditions leading to deposition of naphthalene in mains and services were discussed, and an experiment was shown demonstrating the obstructive effect of one-hundredth part of a pound of naphthalene. In dealing with ammonia recovery, the lecturer compared the ordinary washing process with the processes for the direct productions of sulphate of ammonia which are used in connection with recovery coke-ovens and in a few gas works. The extraction of cyanogen from coal-gas by the Beckton or Bueb, the Foulis, and the polysulphide processes was next considered, and the successful introduction of a modification of the latter process by P. E. Williams into London gas works recorded. Materials for the removal of sulphuretted hydrogen from gas were exhibited, and their action described. The sensitiveness of lead acetate paper as a test for the presence of sulphuretted hydrogen was shown to vary inversely with the area of the paper exposed to the gas.

The sulphur impurity remaining in gas after the extraction of sulphuretted hydrogen was considered by the lecturer to be objectionable on account of its destructive action on the metal work of inverted burners and fittings directly exposed to the undiluted products of combustion of gas. Its relation to the general vitiation of the air of occupied rooms was indicated, and the recent resuscitation in London works of the heated-contact substance process for the removal of carbon disulphide from coal-gas, originally proposed by Dr. A. Vernon Harcourt about 1870, was referred to. In connection with the by-products of gas manufacture, it was stated that the predominant uses of tar at the present time are for the production of pitch for the supply of the patent fuel industry of South Wales, and for road construction and treatment. The lecturer said that physical tests of tar and pitch were misleading as to the value of these materials for the latter purpose, because the physical characteristics changed with efflux of time, and the extent and bearing of the changes which would thus occur in tar and pitch could be ascertained only by appropriate chemical examination of them.

Calorimetry of gas was referred to, the Boys and the Junkers calorimeters being shown in action. The lecturer then drew attention to the acceptance practically everywhere, except in German-speaking countries, of the Harcourt 10 candle pentane lamp, devised primarily for use in gas-testing, as the reference standard of light for all photometric work. The secondary electric standard lamps were calibrated by comparison with it. The stages in the evolution of the present pentane standard by its inventor were indicated by the exhibition of five earlier pentane standards which Dr. A. Vernon Harcourt had successively devised between the years 1877 and 1897, and had discarded in favour of the present standard, which he first described in the latter year. The lecturer stated that he had made comparative tests of the light afforded by about a hundred and fifty different specimens of the Harcourt 10-candle lamp, and had never found disagreement by more than 0·2 per cent, except in cases where a fault in construction had been found. The Hefner standard of light, which is still generally retained in German-speaking countries, was also shown, and the effects of variations in atmospheric conditions on the light of gas and other flames were indi-

cated. The relations subsisting between the several components of more or less diluted products of combustion of town gas were illustrated by curves, and their bearing on questions of the lighting and heating of interiors by means of gas was discussed.

OLD STUDENTS' ASSOCIATION OF THE ROYAL COLLEGE OF SCIENCE.

ANNUAL DINNER, JANUARY 25TH, 1913.

THE Old Students' Association of the Royal College of Science held their Annual Dinner at the Café Monico on Saturday, the 25th ult. Sir WILLIAM CROOKES, President of the Association, occupied the Chair, and the guests included Sir Alfred Keogh, K.C.B.; Sir Henry Miers, F.R.S.; Sir Robert Morant, K.C.B.; Lt.-Col. Sir David Prain, C.I.E.; Sir Lewis Selby-Bigge, K.C.B.; Dr. R. T. Glazebrook, F.R.S.; and Dr. H. Frank Heath, C.B.

After the loyal toasts, Sir DAVID PRAIN proposed "The Royal College of Science and the Old Students' Association." He said one could not help admiring the vitality of the College, which had enabled it to maintain its individuality and the harmony with which it had co operated with the two sister colleges, the School of Mines and the City and Guilds College, in the great work to which they were all devoted.

Sir WILLIAM CROOKES, in replying, said: — When I look around and compare the date (1848) attached to my own name with that of the one next following (Sir W. Tilden, 1860) I feel somewhat staggered at my temerity in accepting the honourable position I occupy. It is nearly sixty-five years since I entered the Royal College of Chemistry. The memory of those early years carries me into what is now considered the Scientific Dark Ages.

To exceed the Psalmist's limit of fourscore years is to be left solitary as regards early friendships. My old friend John Spiller, so far as I can ascertain, is the last of the band of researchers in the early fifties who worked with me at the Royal College of Chemistry.

The state of Science when I was a student was not quite so backward as is generally supposed. Wireless telegraphy, bacteriology, spectrum analysis, and radium were unknown, but other discoveries of world-wide importance were at least in embryo. Wheatstone was at work on the electric telegraph; and Faraday, earnestly on the track of magneto-crystallic force, was grappling with the magneto electric machine—parent of the modern dynamo and of electric lighting. Faraday was first to draw attention of physicists to the highly insulating properties of gutta-percha. He said it was equal to that of the transparent cuticle left behind when an ethereal solution of gun-cotton was allowed to evaporate on a glass plate. The same great chemist was experimenting in low temperatures; I remember seeing him freeze mercury in a red-hot crucible, throw the solid lump on to an anvil, and hammer it out before it melted. Grove, also in the field, had decomposed water by heat alone into its constituent gases, and Joule was determining the mechanical equiva lent of heat; Ebelman was making synthetic rubies by crystallising alumina under great heat from a glassy solvent, and by suitable modification of flux and coloured oxides, either ruby, sapphire, or Oriental emerald could be made, each with its own true crystalline and optical characteristics.

One memorable incident stands out prominently. I was present at the Royal Society's rooms in Somerset House in 1850, when Faraday demonstrated the magnetic character of oxygen gas. Few Royal Society announcements excited so much enthusiasm as did that paper. In the same year I was at one of Mr. Barlow's "At Homes" after a Friday evening lecture at the Royal Institution. My host introduced me to a young man who had made some interesting discoveries in the high ultra-violet end of the spectrum. He had recently been elected to Newton's Chair of Mathematics in the University of Cambridge, and as we both had been working on similar spectrum phenomena, he visually and I photographically, the life-long friendship between Sir George Stokes and myself dates from that evening.

Pasteur had already discovered and separated dextro- and lævo-tartaric acid, and he had started that brilliant series of researches on microbic life—researches which have revolutionised the science of medicine. Indirectly Pasteur solved the famous mediæval problem—"How many angels can stand on the point of a needle?" Altering the word "angels" to "devils"—I have found that, of one of the deadliest diseases that has ever scourged mankind, no less than 500 of the maleficent microbes—veritable devils—could, without overcrowding, find place on the point of the finest needle.

And at that early date scientific men were investigating the chemistry and physics of photography which had recently been started by Daguerre and Nièpce de Saint-Victor in France, and Fox Talbot in England. The production of photographs of natural objects and of the solar spectrum in their true colours was brought to a successful result by Ed. Becquerel. Those who, like myself, had the advantage of seeing Becquerel's colour photographs in their early perfection will agree that they did not fall far short of the recent productions of Lippman. Unfortunately these reproductions could not be handed down to the present generation. The means of permanently fixing them had not been discovered. Increased sensitiveness induced by slight chemical alterations in the ordinary sensitive surface had been discovered, and in the early fifties I saw the photographing of a rapidly moving wheel in about the 100,000th of a second, every spoke in the picture being sharp and distinct as if it had been stationary.

But this extreme sensitiveness was not a general rule. Some of my friends whose portraits I wished to secure were victimised by five-minute sittings in full sun. I took some of the early stereoscopic photographs for Sir Charles Wheatstone, and for nearly sixty years I have seldom gone on holiday without a stereoscopic camera. Many a time my life-long companion on these excursions sat for her portrait against a tree for ten, fifteen, or twenty minutes to give life to a landscape.

In the fifties Becquerel and Röntgen-rays were unknown, but Nièpce de Saint-Victor discovered one of the fundamental properties of uranium. He drew a design on card with a solution of uranium nitrate and exposed it to the sun. After insolation he placed it in the dark, face downwards on a sheet of sensitive paper, with the result that the uranium design impressed its own image.

In those days organic chemistry was almost unknown. To day how great the difference! A chemist is no longer a mere analyst, but an architect and builder, able to manipulate the plastic molecules—to imitate, and even to improve the structure and physiological action of natural products. To the chemist to-day a knowledge of almost every department of natural science is indispensable. If I may look forward as well as backward I should say that the practical side of the chemistry of the future will be synthetic. Already we have synthetic drugs, synthetic scents and essences, synthetic rubber, synthetic dyes, synthetic foods, and alas! synthetic drinks. But we have not yet achieved synthetic beef nor synthetic mutton. I fear I shall not be present at an Old Students' Banquet where these delicacies are served! On the philosophic side of chemistry I predict the greatest progress will be made in enquiries into the constitution of Matter. Even now we are beginning to prick the bubble of those variable, mysterious, and complex things called Elements. At the present day the ideas of the non-elementary character of "elements"—ideas which have been floating about in our minds, *inter apices philosophiæ*, like helium in the sun—may now conceivably be tested in mundane laboratories and used as working explanations of undoubted facts. Science grows and grows. There is no high-water level, no terminal pillar marked "Finis." Our feet will

never fully tread "The pathway to Reality." I exult in the glorious achievements of Science, and when I can no longer take an active part, I still may dream of wonders to come, of future conquests to be won by others.

But I must not forget the object with which I started—to give thanks to the proposer of the toast, "The Royal College of Science and the Old Students' Association," and to reciprocate in the heartiest manner, in the name of all the Old Students here present and of those unavoidably absent, and especially for myself, the ardent wish that prosperity and good fellowship may be our lot so long as these annual dinners continue to be held.

The toast of "The Guests" was proposed by Miss Ethel Thomas.

Sir R. Morant, in replying, spoke of the epoch-making changes which, he believed, were going to take place in the development of the College and of London education generally. They all knew what was in the air. Great changes were needed and must come. They would all agree as to the need for improvement in the correlation of the many activities in the educational whirlpool of London. Obviously the College of Science was to be one of the great, strong, elements of a vivifying kind in the higher education of London, and it would serve that purpose best if it welcomed the assistance of others whose aim was similar—putting on one side sectional jealousies and the mistaken view of *esprit de corps* that no other body could be fit to share and co-operate. Let them, as an Association of Old Students, determine, whatever the circle in which they moved, to develop a realisation of the fact that it was an important duty to take this step forward in the organisation, on the higher plane, of the education of the Metropolis of the Empire. As a body of students they could do much to help public opinion to realise first the enormous need and then the enormous benefit which would be brought about by warm-hearted co-operation among the various elements, elements which must combine if the change was to be the huge success which he believed it would be.

Mr. James Whitehead proposed the toast of the Chairman, and Sir William Crookes replied.

Between the toasts were songs and music. The singers were Lullum Bathurst, Esq., M.D., and James C. Philip, Ph.D., M.A.

NOTICES OF BOOKS.

Theories of Solutions. By Svante Arrhenius. New Haven: Yale University Press. London: Oxford University Press. 1912.

The lectures contained in this book were delivered at Yale University in 1911, and constituted the eighth series of Silliman Memorial Lectures. In them the lecturer endeavoured to put before his audience some of the unsolved problems of the theory of solutions, to show in what directions research work is still needed, and to bring before their notice facts, especially from the work of the older investigators, which are perhaps not generally known. The lectures were addressed to an audience which might be supposed to be thoroughly well acquainted with the principles of physical chemistry, and may be regarded as supplementary to the usual text-books. Professor Arrhenius answered some objections which have been brought forward against the theory of ionisation, or pointed out how the apparent discrepancies might be reconciled, and passed in review all the important work which has been done on solutions in Europe as well as in America.

Die Existenz der Molekule. ("The Existence of Molecules"). By The Svedberg. Leipzig: Akademische Verlagsgesellschaft. 1912.

This monograph deals with the experimental proofs of the existence of molecules, and is in the main a description of the author's own work, that of other investigators being alluded to usually only in so far as is necessary for the complete understanding of Prof. Svedberg's experiments. At the same time some account is given of the history of the controversy about the existence of molecules, and early work on the Brownian movement, for instance, is fairly fully discussed. The first section is devoted to the absorption of light in colloidal and molecular solutions and to diffusion. Colorimetric methods of measurement are first treated, the apparatus being described and full tables of results given. Spectrophotometric experiments performed with gold, selenium, indigo, aniline blue, indophenol, and azobenzene are then discussed, and again the conclusion drawn from them is that discrete particles or molecules exist in molecular solutions. The second section of the book deals first and at considerable length with the Brownian movement, and secondly with the spontaneous variations in concentration in radioactive solutions and gases, which the author has made the subject of special investigations.

Le Froid Industriel et ses Applications. ("Cold and its Industrial Applications"). Second Edition. Paris: Bibliothèque Pratique du Mois Scientifique et Industriel. (2 fr. 75).

This pamphlet, which has reached its second edition, contains detailed descriptions of freezing machines of all kinds which have found application commercially. Some account is given of the evolution of them from the earliest types, and methods of refrigeration are discussed fully. The application of the low temperatures obtained by means of these machines in the cooling of liquids, air, &c., are described, and descriptions are given of the production of ice and the cold storage of various food substances. An interesting section deals with the transport of frozen and chilled viands, and full statistics are given. The use of low temperatures in scientific work is not passed over in the pamphlet, though it is treated only very briefly.

MISCELLANEOUS.

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 3rd inst., the Duke of Northumberland, President, in the Chair. Dr. Edward G. Acheson and Mrs. Norman Thompson were elected Members. The Honorary Secretary announced the decease of M. L. P. Cailletet, an Honorary Member of the Royal Institution, and of Sir George H. Darwin, K.C.B., a Member, and Resolutions of condolence with relatives were passed.

MEETINGS FOR THE WEEK.

Monday, 10th.—Royal Society of Arts, 8. (Cantor Lecture). "The Art of Miniature Painting," by Cyril Davenport.

Tuesday, 11th.—Royal Institution, 3. "The Heredity of Sex and some Cognate Problems," by Prof W. Bateson, F.R.S.

Wednesday, 12th.—Royal Society of Arts, 8. "New Sources of Supply for the Manufacture of Paper," by Clayton Beadle and Henry P. Stevens.

Thursday, 13th.—Royal Institution. 3. "The Dawn of Empire in Shakespeare's Era," by Sir Sidney Lee, LL.D., &c.

—— Royal Society. "A Cassegrain Reflector with Corrected Field," by R. A. Sampson. "Studies of the Processes operative in Solutions—XXV., The Influence of Non-electrolytes on Solubility, the Nature of the Processes of Dissolution and Precipitation," by H. E. Armstrong and J. V. Eyre." "Studies of the Processes operative in Solutions—XXVI., The Disturbance of the Equilibrium in Solutions of Fructose by Salts and by Non-electrolytes," by E. E. Walker. "The Excitation of γ-Rays by the α-Rays of Ionium and Radiothorium," by J. Chadwick and A. S. Russell.

—— Royal Society of Arts, 4.30. "Kathiawar," by Sir Willian Lee-Warner, G.C.S.I., &c.

Friday, 14th.—Royal Institution, 9. "New Gyroscopes and their Applications," by Prof. Andrew Gray, F.R.S., &c.

Saturday, 15th.—Royal Institution, 3. "The Properties and Constitution of the Atom." by Prof. Sir J. J. Thomson, O.M., F.R.S., &c.

THE CHEMICAL NEWS.

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RECENT PROGRESS IN ORGANIC ARSENIC COMPOUNDS.

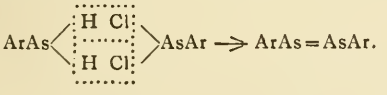
By E. de BARRY BARNETT, B.Sc., A.I.C.

(Concluded from p. 63).

The Arseno-Compounds.

Formation. — The most important reaction leading to the arseno-compounds is the reduction (*Ber.*, xiv., 912; xv., 1952; xliv., 1260, 3293, 3578; xlv., 2130; D.R.P., 206057, 206456, 212205, 216270, 224953, 235430, 244789) of the arsonic acids or arsenoxides: $2ArAsO_3H_2 + 8H = ArAs = AsAr + 6H_2O$. The reduction can be carried out with tin and hydrochloric acid, stannous chloride, or sodium hydrosulphite in neutral solution. The last of these usually gives the best results and is applied in the presence of magnesium chloride. Unsymmetrical arseno compounds can be obtained by the simultaneous reduction (*Pat. Anm. Kl.*, 12, *q.* F 32187, 33163) of two arsonic acids or arsenoxides, provided that these contain a salt-forming group, or of a mixture of an arsonic acid and an arsenoxide, provided that one at least of these contains a salt-forming group, such as an amino- or a hydroxy-group.

Both symmetrical and unsymmetrical arseno-compounds can be obtained by condensing a primary arsine with an arsenoxide or arsen dichloride (*Pat. Anm. Kl.*, 12, *q.* F 31704):—



The arseno-compounds are of especial interest owing to their curative action in the treatment of diseases of protozoal origin, such as syphilis and sleeping sickness. The best known member of the series is 3 . 3′-diamino-4 . 4′-dioxy-arseno-benzene, which has acquired considerable reputation under the name of "Salvarsan" or "606." It can be obtained in several ways, *e.g.*, *p*-oxy-phenyl arsonic acid, obtained by the action of arsenic acid on phenol or from arsanilic acid by the diazo reaction, can be nitrated and the nitro-acid reduced to salvarsan, or *ortho*-nitraniline can be arsonated and then the amino-group replaced by hydroxyl by means of caustic potash.

Properties.—The simple arseno compounds are colourless substances which are insoluble in water. The entrance of an amino- or a hydroxyl group is accompanied by the production of a yellow colour and, of course, renders the arseno-compound soluble in acid or alkali. The amino-arseno-compounds are characterised by giving insoluble sulphates.

The arseno-compounds are very easily oxidised, and this is especially true of the amino- and hydroxy-derivatives. Thus salvarsan is oxidised so readily by the air that it is placed on the market in sealed capsules filled with nitrogen. The products of oxidation are arsenoxides and arsonic acids, and these are readily obtained by the action of hydrogen peroxide.

The arseno-compounds can only be obtained crystalline with difficulty, and show great tendency to form waxes. Only the simpler members have sharp melting-points, the majority decomposing when heated with the production of tri-aryl arsines and free arsenic.

On treatment with halogens the double bond undergoes scission with the production of arsendichlorides, which in the presence of excess of halogen pass into the tetrachlorides. Heating with sulphur also causes rupture of the double bond with the formation of sulphides.

The Dihydroxyarseno-compounds.

These have the structure ArAs[OH]—[HO]AsAr, and are very little known. Up to the present, the di-*p*-amino-compound is the only one that has been isolated. It is said to be obtained by the reduction of the corresponding arsenoxide with sodium amalgam and methyl alcohol (D.R.P., 206057) and described as forming a flocculent yellow mass, melting at 227°. The existence of the compound must be regarded as doubtful, as Ehrlich and Bertheim (*Ber.*, xliv., 1262) have obtained only the arseno-compound on reducing the arsenoxide with sodium amalgam.

The Arsines.

The primary arsines were first obtained by Palmer and Dehn (*Ber.*, xxxiv., 3589) by reducing the arsonic acids with zinc amalgam and hydrochloric acid. They only prepared a few of the simpler compounds, and found that they formed unstable oils with powerful odours and which were very poisonous. Lately it has been found that those primary arsines which contain salt forming groups are much more stable, are less poisonous, and are less readily oxidised in the air. Also they have a powerful effect on trypanosomes, which the simpler members lack. They can be obtained by the exhaustive reduction of the arsonic acids (D.R.P., 251571), arsenoxides, or arseno-compounds with tin, iron, or zinc, and hydrochloric acid.

The secondary arsines are much more sensitive to atmospheric oxidation than the primary compounds. They can be obtained by the reduction of the arsinic acids. Owing to their instability they are of but little interest.

The Tertiary Arsines are better known than either the primary or secondary compounds. As a rule they are fairly stable crystalline substances, which are unaffected in the air. As a rule they are odourless, but some of the mixed derivatives have a disagreeable odour. They are readily obtained, frequently in almost quantitative yield, by the action of sodium on an ethereal solution of the aryl halide and arsenic trichloride. They can also be obtained by the action of arsenic tri-chloride or arsenious acid on magnesium aryl halides (Grignard's reagent), and frequently appear among the decomposition products of other organo-arsenic compounds, *e.g.*, when arseno-compounds are heated. They have no basic properties and are insoluble in acids, but give insoluble addition compounds with platinum chloride and mercuric chloride. They combine with halogens to form dihalides, R_3AsHlg_2, with oxygen to form oxides, $R_3As=O$, and with sulphur to form sulphides, $R_3As=S$.

The Arsonium Salts and Arseno-betaines.

The tertiary arsines are capable of uniting with alkyl iodides to form arsonium salts, R_4AsI (*Annalen*, cccxx., 284). The reaction, as a rule, takes place easily with methyl iodide, less readily with ethyl iodide, and not at all with the higher alkyl iodides. Tri *m*-tolyl arsine, however, reacts very easily with alkyl halides, and even readily with benzyl chloride (*Annalen*, cccxxi., 220).

The arsonium salts are analogous to the ammonium salts, and are derived from strong bases. The iodides are capable of uniting with chlorine to form dichlorides, $R_4ASI<^{Cl}_{Cl}$ (*loc. cit.*).

The arsonium bases are obtained when the arsonium salts are decomposed by silver oxide. They are capable of displacing ammonia from its salts and of absorbing carbon dioxide from the air.

If a tertiary arsine is made to unite with monochloracetic acid, and the arsonium salt then liberated by means of silver oxide, loss of water takes place with the forma-

tion of an arseno-betaine (*Ber.*, xxii., 1567; *Annalen*, cccxx., 276; cccxxi., 174)—

$$R_3As<^{Cl}_{CH_2COOH} \rightarrow R_3As<^{OH}_{CH_2COOH} \rightarrow$$

$$R_3As<^{O}_{CH_2}>CO$$

The Arsen-halides.

Compounds $ArAsCl_2$ are obtained when aromatic compounds react with arsenic tri-chloride. Thus when a mixture of benzene and arsenic tri-chloride is passed through a red-hot tube (*Annalen*, cci., 193), phenyl arsendichloride, $PhAsCl_2$, is formed. This reaction is not assisted by aluminium chloride as might be expected. Dimethyl aniline reacts with arsenic tri-chloride with great ease, *p*-dimethylamino-phenyl arsendichloride being formed in good yield when dimethyl aniline is heated on the water-bath for two hours with arsenic tri-chloride (*Annalen*, cclxx., 139; *Ber.*, xli., 1514). Primary amines when treated in the same way give only addition products, $3ArNH_2.AsCl_3$.

The dichlorides are also readily obtained by the action of arsenic tri-chloride on mercury diaryls (*Annalen*, cci., 196; *Ber.*, cccxx., 272), $Ar_2Hg + AsCl_3 = 2ArAsCl_2 + HgCl_2$, by the action of arsenic tri-chloride on tertiary arsines, $Ar_3As + 2AsCl_3 = 3ArAsCl_2$, and by the action of concentrated halogen acid or phosphorus tri-chloride on the arsenoxides.

The arsendichlorides are stable compounds which distil unchanged and are only slowly attacked by water. They are readily attacked by sodium carbonate to form the arsenoxide, and combine with primary amines to form compounds (*Annalen*, cccxx., 292) $ArAs<^{NHR}_{Cl}$, of the type which are very sensitive to moisture. They unite with chlorine to form tetra-chlorides, $ArAsCl_4$, which are easily decomposed by water to form, first, the oxy-chloride, $ArAsOCl_2$, and then the arsonic acid.

Compounds Ar_2AsCl are obtained by the action of arsendichlorides on mercury diaryls (*Annalen*, cci., 221), $2ArAsCl_2 + HgAr_2 = HgCl_2 + 2Ar_2AsCl$. They are not attacked by water, and are only slowly attacked by aqueous alkali. They are rapidly hydrolysed by alcoholic alkali.

Compounds of Ar_3AsCl_2 are obtained by treating the triaryl arsines with chlorine. With water these give the stable oxy-chlorides, $Ar_3As<^{OH}_{Cl}$, which with caustic alkali pass into the oxides, Ar_3AsO.

The Arsen-sulphides.

The mono-sulphides ArAsS and $[Ar_2As]_2S$ are obtained from the corresponding oxides by the action of sulphuretted hydrogen in alkaline solution. They are well crystalline bodies of feeble acid reaction and are soluble in caustic alkali and polysulphide solutions.

A large number of *arsen-polysulphides* are known. Thus when an arsonic acid is treated with sulphuretted hydrogen and ammonia a salt, $ArAsS[SAm]_2$, is formed. These, again, are unstable, and usually pass into the polysulphide, $ArAs{=}S$ / $ArAs{=}S$ $>S$. All these sulphides are of very minor importance.

Therapeutic Action of Organic Arsenic Compounds.

In preparing a therapeutically valuable arsenic compound it is necessary to obtain one that is very toxic to the parasites, but only slightly toxic to the host. At the same time the substance should be readily soluble in water to form a solution which is neither strongly acid nor strongly alkaline, and which can be sterilised by boiling without fear of decomposition. The substance should be fairly stable so that it can be stored without fear of the formation of poisonous decomposition products.

One of the chief difficulties in treating diseases of protozoal origin lies in the fact that the parasites very readily acquire immunity to the drugs used, and will then tolerate large doses. A culture of parasites which has become immune to one drug is found to be immune to other drugs of the same chemical nature, but not to drugs which are chemically of a different class. Thus, if a culture of trypanosomes is rendered immune to, say, atoxyl, it will be found to be immune to other arsonic acids, but not to arseno-compounds, mercury salts, antimony compounds, &c. By treating such a culture with another specific, say, with trypan red (an azo-dye prepared from tetrazotised benzidene, mono-sulphonic acid, and two molecules of β-naphthylamine-2.6-disulphonic acid) it will become immune to another class of compounds, in this case to azo dyes. Such a culture can then be rendered immune to a third class, and so on (*Ber.*, xlii., 17).

This facility for acquiring immunity renders it necessary to use substances which have such a low toxicity for the host that large doses can be given so as to destroy the parasites before they can become immune. It also makes it advisable to follow up one remedy by another of a different class so as to destroy any parasites which may have acquired immunity to the first; *e.g.* to follow up salvarsan with mercury.

Bunsen recognised that cacodylic acid is relatively non-toxic, and this was latterly introduced into medicine in various forms, such as the sodium salt and guaiacol salt.

At a later date this was replaced by sodium methyl arsonate ("arrhenal" or "new cacodyl"), but neither of these was very successful.

Greater success was obtained by the use of the sodium salt of arsanilic acid. As pointed out above, this was believed to be an anilide of arsenic acid, and was introduced into medicine as its sodium salt under the names of "atoxyl," "soamine," and "arsamine." The drug was usually administered subcutaneously, but was also sometimes given *per os*. It met with some success in the treatment of syphilis and sleeping sickness, but suffered from the disadvantage that it could not be sterilised by boiling, and that it frequently produced blindness. Many attempts were made to obtain a compound of similar structure which, while retaining the trypanocidal properties, would be less toxic to the host. Thus, Wellcome and Pyman arguing that *o*-toluidine is less poisonous than aniline, prepared the arsonic acid from it. This, however, proved to be not less toxic than arsanilic acid. The entrance of halogen into the nucleus was found to increase the toxicity, as was the replacement of the amino group by halogen. Sulphonation, as would be expected, decreases the toxicity, sulphonated arsanilic acid being no more poisonous than common salt, according to Ehrlich. Unfortunately, at the same time it completely destroys the trypanocidal action.

Since some azo-dyes, such as trypan red (see above), have considerable action on trypanosomes, Barrowcliffe, Pyman, and Remfry prepared azo-dyes from toluidine arsonic acid. These, however, proved to have little trypanocidal action. A similar result was obtained when tri phenyl methane dyes containing an arsonic acid group were examined. Thus the dye obtained by condensing tetramethyl-amino-benzhydrol with oxyphenyl arsonic acid has no trypanocidal action, and is less toxic than the unarsenated substance. Here the arsonic acid group acts like the sulphonic and carboxylic acid group in decreasing the toxicity, *e.g.*, salicylic acid is less poisonous than phenol.

Much better results were obtained by substituting the amino-hydrogen atoms in arsanilic acid. If these are replaced by alkyl groups no decrease in toxicity can be observed, but the glycine prepared by condensing with chloracetic acid is much less toxic than arsanilic acid, and at the same time has the same trypanocidal effect. In the acetyl derivative a similar modification of properties is observed, and at the same time the compound has the great advantage that it can be sterilised by boiling and is less

apt to give rise to unpleasant symptoms. The sodium salt of this acetyl compound enjoyed a considerable vogue under the name of "arsacetin" or "orsudan." Other acyl derivatives proved to be as toxic or more toxic than arsanilic acid, the toxicity increasing with the length of the chain and with the presence of benzene nuclei.

The action of the arsinic acids has also been tested, but they have been found to be without effect. The azo-dyes derived from them are also useless.

A very important step in the therapeutics of organic arsenic compounds was made by Ehrlich, who observed that, although a concentration of 1 in 120,000 of atoxyl in the blood is fatal to trypanosomes, the parasites can survive for several hours in a 5 per cent solution of the drug *in vitro*. Obviously the atoxyl must undergo some change in the body. This change Ehrlich considered was probably a reduction to a tri-valent arsenic compound, and this supposition has been amply borne out by experiment. Thus the reduction products of arsanilic acid and its derivatives are efficient both *in vitro* and *in vivo*, *e.g.*, a concentration of the arsenoxide of 1 in 10,000,000 kills all parasites in an hour *in vitro*. This led to the careful investigation of a large number of arsenoxides and arseno-compounds, the most suitable of which was found to be 4-amino-3-oxyarseno-benzene ("salvarsan" or "606"). This compound has a marvellous effect in cases of syphilis, and is comparatively free from unpleasant by-effects. It is placed on the market as the dihydrochloride in evacuated or nitrogen filled capsules. It is usually applied as an intravenous injection, and, as the aqueous solution is strongly acid in reaction, the injection causes considerable pain unless the solution is first neutralised. It is also occasionally applied as an oily emulsion.

SEBACATES AND CACODYLATES OF THE RARE EARTHS.

By C. F. WHITTEMORE and C. JAMES.

THE sebacates appeared to be worthy of special consideration, inasmuch as they afford a separation of the rare earths from thorium in a faintly acid solution and from the alkalis in a neutral solution. The cacodylates seemed especially interesting on account of their characteristic properties.

The Sebacates.

Lanthanum sebacate, $[C_8H_{16}(COO)_2]_3La_2.2H_2O$, was obtained as a white precipitate by adding a solution of ammonium sebacate to a neutral solution of lanthanum chloride. The whole was kept at 100° for a short time, the liquid separated by filtration, and the salt washed first with water containing sebacic acid and finally with alcohol and ether. This compound formed a white voluminous powder, which was soluble in dilute mineral acids and insoluble in water.

The lanthanum oxide was determined by igniting to constant weight, while the carbon and hydrogen were estimated by combustion. The following results were obtained:—

Calculated: La_2O_3, 35·67; H, 5·73; C, 39·40. Found: La_2O_3, 35·63; H, 5·88; C, 39·44.

Praseodymium Sebacate, $[C_8H_{16}(COO)_2]_3Pr_2.2H_2O$.—This substance was prepared in a similar manner to the lanthanum compound. It formed a very pale green voluminous powder, soluble in dilute mineral acids and insoluble in water. The sebacates appeared to form no double salts with ammonium sebacate. The composition of this substance was ascertained by determining the amounts of hydrogen and carbon present.

Calculated: H, 5·71; C, 39·22. Found: H, 5·67; C, 39·43.

Neodymium sebacate, $[C_8H_{16}(COO)_2]_3Nd_2.3H_2O$, was obtained by the method used in the two preceding preparations. It was a light powder of a very pale amethyst colour with properties similar to those of the corresponding lanthanum and praseodymium compounds. A simple ignition gave the following results:—

Calculated: Nd_2O_3, 35·70. Found: Nd_2O_3, 35·60.

After drying at 100° for some time the amount of water of hydration remained practically unchanged.

Samarium sebacate, $[C_8H_{16}(COO)_2]_3Sa_2.4H_2O$, was prepared as described above. This compound formed a nearly white powder, which resembled the former sebacates in its reactions.

By igniting, it was found that the composition corresponded to 4 molecules of water of crystallisation.

Calculated: Sa_2O_3, 35·84. Found: Sa_2O_3, 35·82.

Yttrium sebacate, $[C_8H_{16}(COO)_2]_3Yt_2.4H_2O$, was prepared by adding a solution of ammonium sebacate to the neutral chloride solution, as in the preparation of the former cerium earth compounds. This sebacate consisted of a light white powder, soluble in dilute mineral acids and insoluble in water.

The analysis of this salt showed that it contained 4 molecules of water of crystallisation, which is similar to the amount carried by the samarium compound. This resemblance between yttrium and samarium salts has often been observed before.

Calculated: Yt_2O_3, 26·57. Found: Yt_2O_3, 26·48.

The Use of the Sebacates for the Quantitative Estimation of the Rare Earths.

In a previous paper the authors have shown that yttrium can be quantitatively separated from the alkalis by precipitation with ammonium sebacate. Recently this reagent has been applied to several members of the cerium group, with the following results:—

Lanthanum (a) *from Sodium*.—A solution of lanthanum nitrate was standardised by precipitation with ammonium sebacate, as follows:—Twenty-five cc. of the solution were diluted to about 100 cc., heated to boiling, a slight excess of ammonium sebacate added, and the whole allowed to stand for a short time at 100°. This precipitate was filtered off, washed, dried, and ignited. 25 cc. were found to contain 0·2789 grm. of La_2O_3.

In the same manner, the lanthanum was precipitated from a similar quantity of the standard solution to which 5 cc. of a 10 per cent solution of sodium chloride had been added.

Standard, 0·2789. Found, 0·2791.

(b) *From Potassium*.—Following the procedure described above, lanthanum was precipitated from the same amounts of standard solution to which 10 cc. of a 10 per cent solution of potassium chloride had been added.

Standard, 0·2789. Found, 0·2790.

It will be seen that lanthanum differs from yttrium, inasmuch as it can be separated from potassium by one precipitation.

Cerium (a) *from Sodium*.—The separation of this element was studied in a similar way to the lanthanum. 25 cc. were found to contain 0·1272 grm. CeO_2, and the cerium in like amounts was precipitated in the presence of 10 cc. of 10 per cent sodium chloride solution.

Standard, 0·1272. Found, 0·1274.

(b) *From Potassium*.—In this case potassium chloride was substituted for sodium chloride.

Standard, 0·1272. Found, 0·1275.

Neodymium (a) *from Sodium*.—Neodymium chloride was standardised, and treated as above.

Standard, 0·1474. Found, 0·1475.

(b) *From Potassium.*—It was found that one precipitation gave a complete separation as in the preceding cases.

Standard, 0·1474. Found, 0·1476.

The Cacodylates.

Lanthanum and Cerium Cacodylates.—These salts are extremely difficult to obtain pure, owing to their great solubility. The lanthanum solution readily becomes milky, and it cannot be filtered because of its colloidal nature.

Perhaps the most remarkable property of the rare earth cacodylates is the ease with which they form double salts with rare earth compounds, such as chlorides, nitrates, sulphates, &c. Some of these substances will be described further on.

Praseodymium cacodylate, $[(CH_3)_2AsO_2]_6Pr_2.16H_2O$, was prepared by dissolving praseodymium hydroxide in a boiling solution of cacodylic acid. It is absolutely necessary that the hydroxide be thoroughly washed free from all traces of chlorides, &c., since these impurities would cause the formation of a certain amount of double salts. The solution of praseodymium cacodylate was filtered, evaporated, and allowed to crystallise. The crystals were filtered off and carefully washed with alcohol.

This cacodylate forms pale green crystals, which are soluble in water. One hundred parts of water dissolve 8·43 parts at 25°. Since strong solutions of the more soluble cacodylates form jelly-like masses with alcohol, this reagent cannot be used to throw down crystals of these salts.

In the analysis, praseodymium oxalate was titrated with potassium permanganate.

Calculated: Pr_2O_3, 23·67. Found: Pr_2O_3, 23·46.

Neodymium cacodylate, $[(CH_3)_2AsO_2]_6Nd_2 16H_2O$, was obtained in a similar manner to the praseodymium compound, by using the same precautions.

This salt formed small crvstals of a very pale amethyst colour, soluble in water. One hundred parts of water dissolve 5·13 parts of the compound at 25°. After heating for some time at 100°, all water of hydration was given off.

Calculated: Nd_2O_3, 24·05; H_2O, 20·61. Found: Nd_2O_3, 24·19; H_2O, 20·39.

Samarium Cacodylate, $[(CH_3)_2AsO_2]_6Sa_2.16H_2O$.—This cacodylate was prepared and described in an earlier paper.

It forms nearly white crystals, which are very soluble in boiling water and much less in cold. One hundred parts of water at 25° dissolve 1·60 parts of the cacodylate.

Yttrium Cacodylate, $[(CH_3)_2AsO_2]_6Y_2.18H_2O$. — A boiling neutral solution of yttrium chloride was treated with a slight excess of sodium cacodylate. A precipitate of the yttrium salt soon formed. The mass was kept at 100° for some time, when practically all of the yttrium was thrown out of solution. The crystalline precipitate was washed with hot water containing a little cacodylic acid; finally, alcohol removed the small amount of acid remaining. In this case the presence of a chloride does not affect the purity of the compound, since the normal cacodylate is less soluble than the double salt.

Yttrium cacodylate forms a powder of small white crystals, which are only very slightly soluble in boiling water and insoluble in cold. The salt became anhydrous at 100°.

Calculated: Y_2O_3, 17·07. Found: Y_2O_3, 17·16.

Thulium Cacodylate, $[(CH_3)_2AsO_2]_6Tm_2.16H_2O$.—This was prepared by heating thulium hydroxide with a solution of cacodylic acid. A crystalline powder formed, which was separated by filtration and washed.

This salt is nearly insoluble in boiling water.

Thalium cacodylate was shown to possess sixteen molecules of water of crystallisation, by heating to 100° and weighing the anhydrous salt.

Calculated: H_2O, 19·91. Found: H_2O, 19·81.

Fractionation by means of the Cacodylates.

The material first studied was rich in yttrium, dysprosium, and holmium. The crude oxides were dissolved in hydrochloric acid, the solution diluted and precipitated with oxalic acid. The oxalates were washed, dried, ignited, and dissolved in hydrochloric acid. A neutral solution was obtained by gradually adding the acid drop by drop towards the end of the reaction. The chlorides were diluted, heated to boiling, and stirred rapidly by a motor. Sodium cacodylate was slowly added, causing at first no precipitate, owing to the formation of double salts. After a time the normal cacodylates were deposited as a crystalline powder. When a sufficient quantity had formed, it was separated by filtration, the liquid was returned to the beaker, and again submitted to the same process. In this way four fractions were obtained. The oxide from Fraction 1 was coloured yellowish, and was richer in yttrium than the original material. Fraction 4, obtained by precipitating the filtrate from Fraction 3, by means of oxalic acid, gave upon ignition an orange-brown oxide. A nitric acid solution of this oxide gave absorption bands of neodymium, dysprosium, and holmium. Practically all the rare earth metals from lanthanum to samarium were concentrated in this last fraction. It was also rich in gadolinium, and contained most of the terbium of the original crude oxides. Owing to the presence of neodymium it was difficult to observe whether there had been any separation between holmium and dysprosium.

Finally, material consisting chiefly of neodymium, samarium, and gadolinium was employed. The hydroxides were boiled with cacodylic acid, and the resulting cacodylates fractionated by boiling out with water and crystallising by evaporation. Neodymium rapidly collected in the more soluble portions, while nearly all the terbium and dysprosium remained in the portion only slightly soluble in cold water. Although the neodymium compound is very soluble in boiling water, it tends to cling somewhat to those elements forming slightly soluble cacodylates.

Double Salts.

Lanthanum Chloride Cacodylate,—

$$2La[(CH_3)_2AsO_2]_3.LaCl_3.18H_2O.$$

—Lanthanum cacodylate forms double salts with the sulphate, nitrate, chloride, bromide, iodide, methanetrisulphonate, &c., of lanthanum. Although lanthanum cacodylate and lanthanum nitrate are both very soluble in water, their dilute solutions, upon mixing, give a precipitate which is nearly insoluble.

When solutions of lanthanum chloride and the cacodylate are mixed, a double salt rapidly separates as a mass of fine crystals. These were filtered off, washed, dried, and analysed. The results showed that one molecule of lanthanum chloride united with two molecules of lanthanum cocodylate.

Calculated: La_2O_3, 29·28; Cl, 6·37. Found: La_2O_3, 29·43; Cl, 6·24.

Cerium Chloride Cacodylate,—

$$2Ce[(CH_3)_2AsO_2]_3.CeCl_3.18H_2O.$$

—This compound separated upon mixing solutions of cerium chloride and cerium cacodylate. It consisted of white fibrous crystals. The CeO_2 content showed that its composition resembled that of the corresponding lanthanum salt.

Calculated: CeO_2, 30·87. Found: CeO_2, 30·88.

Cerium Sulphate Cacodylate was obtained as a thick precipitate by mixing the sulphate and cacodylate solutions. The mass filtered badly, but was finally washed and dried. The analysis indicated that it probably consisted of one molecule of cerous sulphate in combination with half a molecule of cerous cacodylate.

Neodymium Chloride Cacodylate,—

$$2Nd[(CH_3)_2AsO_2]_3.NdCl_3.18H_2O,$$

was prepared in a similar manner to the double chlorides described above. It formed very pale amethyst crystals, which were of a fibrous nature.

Calculated: Nd_2O_3, 30·00; Cl, 6·31. Found: Nd_2O_3 30·04; Cl, 6·31.

Durham, N.H.

ON THE DENSITY OF SOLID SUBSTANCES, WITH ESPECIAL REFERENCE TO PERMANENT CHANGES PRODUCED BY HIGH PRESSURES.*

By JOHN JOHNSTON and L. H. ADAMS.

(Continued from p. 65).

The After-Effect of Pressure on the Density of Solids.

For the experiments on the residual effect produced by very high hydrostatic pressures on the density of homogeneous crystals, we again used potassium sulphate, of size between 40 and 60 mesh. This size was chosen simply for the sake of convenience of manipulation, for from the preceding paragraphs it is evident that the effect of pressure does not depend upon the size of the crystal, so long as the material is strictly homogeneous.

The pressure bomb, of which a drawing to scale is given in Fig. 2, is of vanadium steel; it is 6 inches in length,

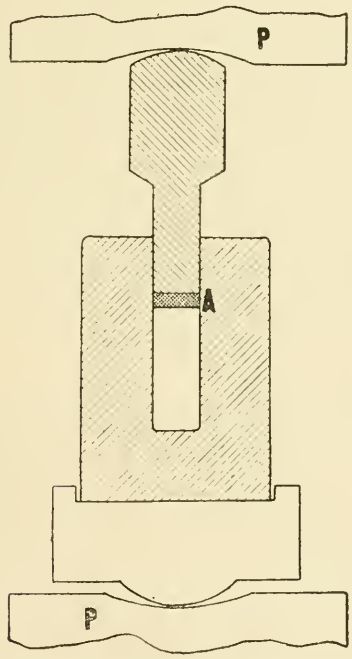


Fig. 2.—Shaded parts represent the bomb and plunger to scale; the other parts represent diagrammatically the press, platens P P, and the arrangement by means of which the bomb centres itself as pressure is applied to the plunger. A is the slice of rubber stopper.

4 inches in internal diameter, with 1 inch diameter of bore. The plunger, of glass-hard steel, is a slip fit, but leak of oil past the plunger is prevented by the slice of soft rubber, A. Pressure was applied by means of a 500 ton hydraulic press, of which the platens are represented by P P in the figure. The figure also shows the arrangement by means of which the bomb centres itself. Without some such arrangement as this, it is next to impossible to obtain a rectilinear thrust parallel to the axis of the bomb; and, if this condition does not hold, leaks soon develop, and can be cured only by enlarging the bomb and by grinding a new and somewhat larger plunger to fit it.

The procedure was as follows:—A quantity of about 10 grms. of the substance was, in the earlier experiments, enclosed in a little bag of thin sheet rubber, the mouth of which was then tied tightly; but, as it was found impossible wholly to exclude the liquid used for compression, in the later experiments the substance was just placed within a copper tube, 1 cm. in diameter, closed at one end. The vessel containing the material was placed in the bomb and surrounded by paraffin oil (or by aqueous glycerol in some cases); the plunger was inserted, and the pressure was applied by means of a hydraulic press and continued for an hour or longer. The amount of pressure was calculated from the total compressive force exerted by the press, as measured on a hydrostatic gauge; the values given are only approximate, as no allowance was made for friction; they cannot, however, be in serious error. After the release of the pressure, the material was well washed with gasoline to remove the paraffin oil, and after heating for half an hour to 200°, its density was determined as described above. The results follow:—

Table V.—*After-Effect of High Pressure on the Density of* K_2SO_4.

Density before compression	2·6574
Density of one sample of same after 1 hour at 10,000 atmospheres	2·6563
Density of a second sample of same after 1 hour at 15,000 atmospheres	2·6558

Here again the differences are of the same magnitude as the error of experiment; again, however, it may be noted that the change, if it exists at all, is a decrease.

Spring (*Bull. Acad. Roy. Belg.*, 1883, [3], vi., 507) in his experiments on the after-effect of pressure on specific gravity of solids, compressed gradually in the dry state without the use of oil; the substance was subjected to pressure for a period of about three weeks, and after its density had been determined, to a second compression lasting some days. The amount of pressure was calculated to be some 20,000 atmospheres, but was probably considerably less, owing to the great friction incidental to such a method of compression. His experimental results on salts are contained in Table VI.

Table VI.—*Spring's Results on the After-Effect of Pressure on the Density of Salts.*

	Before compression.	After first compression.	After second compression.	Mean change produced by compression.
KCl ..	1·980	2·071	2·068	+0·090
KBr ..	2·505	2·704	2·700	+0·197
KI	3·012	3·110	3·112	+0·099
K_2SO_4 ..	2·653	2·651	2·656	0·0
$(NH_4)_2SO_4$	1·773	1·750	1·760	−0·018
NH_4 alum	1·641	1·629	1·634	−0·009
K alum ..	1·758	1·756	1·750	−0·005
Cs alum ..	1·988	2·000	2·005	+0·014
Cr alum ..	1·828	1·823	—	−0·005
Tl alum ..	2·320	2·314	2·314	−0·006

This shows that the differences between the density after the first and that after the second compression are small and irregular; hence they are doubtless due to experimental error, which, to judge from the procedure employed, could easily have amounted to 0·005. The mean changes produced by compression are large and positive for the halides of potassium, just as one would expect from a microscopical examination, which shows that the crystals of all three substances are usually no

* From the *Journal of the American Chemical Society*, xxxiv., No. 5.

homogeneous, but contain small holes and flaws; with the other substances, excepting ammonium sulphate and cæsium alum, the changes are hardly greater than the probable experimental error, while with potassium sulphate there was no change, in agreement with what we have found. On account of the anomalous change in density of ammonium sulphate found by Spring, we investigated the effect of hydrostatic pressure on the density of this substance; the procedure was identical with that described above except that prior to the determination of the density some of the samples were heated to 115° for half an hour; others, however, were dried in a vacuum desiccator and not heated at all. The results, presented in Table VII., of both sets of experiments are concordant, and show again that no after-effect has been produced by pressure.

TABLE VII.—*Influence of Pressure on the Density of* $(NH_4)_2SO_4$.

(*a*) Samples heated to 115° before determination of the density.	
Before compression	= 1·7655
After 2 hours at 12,000 atm. ..	= 1·7671
(*b*) Samples unheated.	
Before compression	= 1·7637
After 1 hour at 8000 atm.	= 1·7639

From the foregoing it is evident that the change of density observed after powdering a well-defined crystalline substance, or subjecting it to pressure, is in the direction of an increase only when the original substance contained cracks or holes; that is to say, an increased density is due entirely to accidental circumstances; with strictly homogenous crystalline substances, on the other hand, the change of density is usually less than 0·001, and, if real, is in the direction of a decrease.

(To be continued).

THE BIRTH OF THE ATOM.*

THE Chemical Society, meeting on February 6th, at its rooms in Burlington House, opened its Proceedings by considering two remarkable papers, the first by Sir WILLIAM RAMSAY on the presence of helium in an X-ray bulb, and the second by Prof. NORMAN COLLIE, of University College, London, and Mr. H. PATTERSON, of the University of Leeds, and late of University College. Briefly the papers may be described as a notable contribution to the newer school of physics, and the conclusion to be drawn from them is that the authors claim to have done one of two things, either to have achieved clearly and definitely the transmutation of elements or to have evolved matter from energy. At the outset it must be admitted that neither of these claims was put forward in so many words by the authors, but to appreciate the significance of their discovery, of which a full account is given below, it may be well to get a clear idea of current chemical conceptions, both as regards the transmutation of elements and the relation existing between matter and energy.

Essential of the Atomic Theory.

The essential of the atomic theory from the point of view of transmutation was till quite recently that every object known in Nature was either elementary or was built up of a combination of two or more elementary substances. Thus oxygen, hydrogen, carbon were looked upon as elements, because, among other reasons, by no known means could they be split up into anything simpler. Sugar, on the other hand, was regarded as a compound because the chemist is able to break it down into carbon, oxygen, and hydrogen. The instance is a simple one to be verified by the homeliest of apparatus. It is only necessary to heat a lump of sugar. The black mass left over is carbon, and if a cold surface such as a piece of glass is held above the sugar, water, which is a compound of hydrogen and oxygen, can be seen to condense on the surface. Before the atomic theory was formulated it was the dream of the alchemist to transmute the baser into the nobler metals, to turn iron, for instance, into gold, but with the acceptance of the atomic theory the idea was dismissed as unthinkable because the different atoms were looked upon as utterly separate individuals, having no connection one with another—as being, in fact, the final units of which matter was built up. Passing over the suggestive grouping of the atoms by Newlands, Mendeléeff, and others in the Fifties, and the brilliant hypotheses that led men to think that the atoms themselves were universes built up of infinitely complex groupings, one comes to the opening years of the present century, when it was established firstly that radium was an element, and secondly that it was degenerating spontaneously into helium and radium emanation. The credit of the discovery belongs to Sir William Ramsay and Mr. Frederick Soddy, and with it followed a whole host of other transmutations, all of them spontaneous, none of them able to be hastened or retarded. In 1906, however, in a remarkable paper by Mr. Cameron and Sir William Ramsay, the view was put forward that if copper were subjected to the action of radium emanation the element copper could be to some extent broken down into the element lithium. A pictorial analogy can now be made to represent the meaning of transmutation. We may imagine the elements classified into eight groups, having such geometric forms as triangles, squares, pentagons, hexagons, and so forth. There would be some eight triangles, some eight squares, some eight pentagons, and so on, all increasing by progressive stages and built up like the Indian boxes which fitted one within the other. The large box containing all the others behaves as a separate unit, completely hiding the boxes within. Then comes a particle shot out with inconceivable velocity by radium, and shatters the outer box, leaving behind it the remaining boxes intact. The eight-box element has been transmuted into the seven-box element, just as the seven-box element, if its outer case be shattered, into the six-box, and so on down the series. It is a part of elementary chemistry that copper, sodium, and lithium are all elements belonging to a single grouping.

Matter and Energy.

To turn now from transmutation to the concepts of matter and energy. It may be regarded as still being the orthodox view that both matter and energy are indestructible, and that neither can be turned into the other. When coal burns and give birth to energy the coal is not lost but re-appears as the gas carbon dioxide, the energy obtained being what chemists term the energy of chemical combination, or put more popularly, in the specific instance, the recovery of the energy of the sun's rays that were absorbed by the primæval forests, and trapped and preserved when these were compressed into the coal measures. The newer school, however, of which M. Gustave Le Bon is one of the leading exponents, holds that energy and matter are one, that the mysterious ether of the universe appears to our senses as matter when once it is stirred into vortex rings, that the birth of a star is nothing more than the ether set into violent ordered motion, acquiring the properties of matter, much as a smoke ring by virtue of its movement takes on some of the properties of a solid substance. In this view the atom would consist of many thousands of particles, each particle being ether in a whirl and the whole held together by a supreme force. With this as an introduction the experiments described last night come into proper perspective. The authors show that if they send an electric discharge—that obtained as in the cathode rays from an ordinary Ruhmkorff coil—through a vacuum tube containing a little hydrogen, helium and neon

* We take this account of the Procedings of the Chemical Society from the *Morning Post* of February 7th.

make their appearance. This happens in each occasion, regularly, in a short space of time. The gases were not present at the outset of the experiment, the possibility of their being introduced from outside has been rigidly excluded, but two well-known elements have made their appearance as the result of the passage of an electric discharge through a vacuum tube containing hydrogen.

Two Possibilities.

Two possibilities present themselves, and it will be for future experiments to determine which is the correct hypothesis. Either the hydrogen or the elements contained in the glass or in the electrodes have been transmuted into helium and neon, or as a result of the energy of the electric discharge, helium and neon, two elementary material gases, have been created out of immaterial ether.

A final point before the report. Last night's experiments are notably different from the previous ones of Sir William Ramsay. His early discovery of transmutation, that radium broke down into helium, and niton or radium emanation, was an instance of the disruption of the most complex element known, and was in so far comparable with the breaking of a wave when it reaches beyond its critical size. His later experiments were so difficult of reproduction that in his book published this year Prof. Rutherford regards the results as non-proven, Madame Curie and her fellow-workers having attempted to reproduce the phenomenon and failed. Prof. Collie and Mr. Patterson have either transmuted ordinary simple elements into neon and helium or they have created out of the ether elements of extreme simplicity. It is a matter of indifference whether these elements have been built up from the hydrogen in the tube or whether they are built up directly from electrical energy. The point is that if the hypothesis suggested is true the complete life history of the different atoms has been determined experimentally. In the hottest and most recently-formed stars, hydrogen, helium, and possibly one or two other elements not known on the earth, make their appearance, all of them being of small atomic weight. As the stars cool down the atoms become heavier, or in other words, you get the synthesis of atoms. There is some process at work building up the atom that till now has never been realised experimentally, but in the experiments described last night one is apparently assisting at the birth of the atom. The other end of the history, the death of the atom, has already been told in the overloading and disruption of the radium atom, and in consequence the initial and the final episodes in the life history of the atom have, it is thought by many, been experimentally described. Much of the history, it should be added in conclusion, is hypothetical, but there is good reason to believe that the experimental facts reported last night are closely related to the hypothesis.

Meeting of the Society.

Suggested Origin of Neon.

In the absence of the President of the Chemical Society, Prof. Arthur Smithells, Professor of Chemistry at the University of Leeds, presided at the meeting of the Chemical Society at Burlington House on February 6th.

Sir William Ramsay, in his paper on "The Presence of Helium in the Gas from the Interior of an X-ray Tube," reminded the Fellows that some years ago he and Mr. Cameron had obtained lithium from copper, though people were mildly incredulous. (Laughter.) He had also published a statement to the effect that under the influence of radium emanation silicon gave some carbon dioxide, while with thorium a respectable quantity of carbon dioxide was obtained, the inference being that the element tended to break down to carbon, which in the presence of oxygen became carbon dioxide. When the time came for him to have to return the radium that had been lent to him he had looked about for some other substance with which to continue his experiments. Radium gave helium and niton, or radium emanation, and also heat and α-rays. Niton was extraordinarily energetic, more so than any other known substance, so that a cubic centimetre of it gave more than three and a-half million times the energy of a cubic centimetre of explosive gas. During the decomposition of the emanation α-rays were given off and β rays with even greater velocity. The question to determine was whether it was possible to find signs of chemical transformation through the β-rays, a difficult one when it was remembered that only 6 per cent of the energy of emanation appeared in the form of β-rays. He had made the attempt, however, with old X-ray bulbs. In the first instance his method had been to break the bulbs, and on analysing the gases contained in the glass by means of the combustion tube, he had found traces of helium, neon, and argon. Last November, instead of breaking the bulbs, he had heated them to 300° and collected the gases, finding the spectrum of helium and also a small quantity of neon. As a result of these experiments there was no question that the bulbs contained helium. The problem was what was the source of this helium. It might have been derived from the electrodes, or from impact with the cathode or anti-cathode, or from the impact of the cathodic rays with the glass. Last summer he had informed the Society that on treating water with radium emanation, instead of getting helium, neon was got, the equation suggesting itself that helium (4) plus oxygen (16) equals neon (20). Thus at Bath, when the waters were charged with radium, great quantities of both neon and helium were produced.

Results Reached Independently.

Prof. J. Norman Collie and Mr. H. Patterson read their paper on "The Presence of Neon in Hydrogen after the Passage of the Electric Discharge through Hydrogen at Low Pressures."

Prof. Collie drew attention to the fact that he and Mr. Patterson had done the early portion of the work of their joint paper independently and from different points of view, and that it was only in the later stages of the work, when they learnt that they were getting the same results independently, that they had collaborated. He described his early experiments, which had been undertaken on fluorspar with the hope of decomposing the fluorine by means of the electric discharge. On testing some fluorspar that Sir William Ramsay had received from Iceland last summer he had found that helium was given off. Further investigation showed that the spar gave off carbon monoxide and other gases, and when the problem had been investigated with one of Sir William Ramsay's ingenious apparatuses it had been determined that on treating the spar neon was produced. Further investigation showed that the same result was obtained by using calcium chloride, and again by using glass-wool, and then again by carrying out the discharge on the bare glass-tube. (Cheers). What was the origin of the neon? Had air leaked in through the taps of the apparatus? Was it due to impurities in the hydrogen placed in the tube to conduct the current, or to the oxygen used in the later stages to get rid of the hydrogen, or to neon being dissolved in the glass? Prof. Collie described the experiments undertaken to exclude the possibility of there being any such origin for the gas, and also the attempt made with a negative result to see whether the neon could have leaked through the heated glass-tube.

Standpoint of Pure Physics.

At this stage, Mr. Patterson continued the paper, showing the point of view from which he had undertaken the research. He had been interested, he said, in the pure physics of the electron. He described the formulæ on which he had built up a hypothesis, and startled the Fellows by the calm announcement that he had thought it conceivable that by doubling the electrical charge on the hydrogen atom it might be possible to convert this into an α-particle, and so into helium. He did not, he said, regard the result of the experiment as proving the hypothesis, but he thought that perhaps his hypothesis provided an explanation. (Cheers).

Prof. Collie then resumed his reading of the paper, drawing attention to the fact that Mr. Patterson, in sparking hydrogen, had not got helium, but neon. He had, he said, criticised Mr. Patterson's method of preparing hydrogen, and to avoid this possibility of error, Mr. Patterson had started by filling his apparatus with pure oxygen, but on pumping this out had got the same result. Another possibility had then suggested itself. While neon did not enter glass under ordinary conditions, might it not do so under the influence of the X-ray discharge? To make certain on this point the experiment tube was surrounded with another tube containing neon, and about the same result was obtained as with ordinary air. A similar experiment was made with helium with negative results. Lastly, before sending in his paper the previous week, he had used the outside vessel as a vacuum (a higher than an X-ray vacuum), and still the neon appeared, the quantity thus obtained being comparable with that present in about 2 cubic centimetres of air. (Loud cheers).

Startling Discovery.

Last Friday and Saturday, he repeated, he had performed the experiment twice with the experiment tube surrounded by a vacuum. He had then asked himself whether there was anything else he could test. He had nothing particular to do that afternoon, and had decided to test whether there was anything in the outer chamber. He let a cubic centrimetre of pure oxygen into the outer chamber, and he obtained a slight explosion due to hydrogen. He absorbed the oxygen in the usual way with carbon, but there was still some left, which he regarded as rather a nuisance. He repeated the process of absorption, but the gas still remained, in relatively large amount. He decided to test it, and turned on the coil. The sight he then saw astounded him, for the tube was a blaze of helium, with some neon mixed. (Loud cheers). He communicated with Mr. Patterson, who repeated the experiment. Mr. Patterson at first found helium. Then he put oxygen into the outer tube, and he found, instead of helium, a large quantity of neon, the equation being suggested that helium (4) plus oxygen (16) equals neon (20). (Cheers). If the helium had sufficient velocity, when produced in the inner tube, to traverse it, it was quite possible for a new element to be produced. For his own part he was quite satisfied provided neon and helium had been produced from substances in which they were previously not present. (Cheers).

Possible Origin of the Gases.

There were various possibilities. It might be that the elements of the tube in the electrodes gave neon or helium under the influence of the discharge. This gave them ten or a dozen elements to choose from as the source. Again, there was the chance that the hydrogen was the source. Or it was possible that they were dealing with a primordial form of matter, the primordial atom which, when produced, had all the energy necessary for forming the world. By the combination of these "atoms" the atoms of the elements would be found. Helium, and possibly hydrogen, were present in the nebular state, and they were present in the experimental tube. Possibly the electric current directed the flow of these atoms with the full force of its energy, and with the phenomena of heat and light the elements came into existence. At any rate one thing seemed certain. The elements could be changed, and they could be changed in a way very different from the way that radium was changed. In its case the process could neither be hastened nor retarded. But the present phenomenon was artificial, and, further, the process was occurring at the other end of the system of the atoms, producing elements of low atomic weight. The old idea of the transmutation of elements had to be altered. We were coming now to know more of sub-atomic matter, and had to be realised that—

> The old order changeth, yielding place to new,
> And God fulfils Himself in many ways
> Lest one good custom should corrupt the world.

Prof. Collie then showed two beautiful illustrations of the effect of sparking neon, the gas when absolutely pure blazing out into a pillar of perfect flame red. He added, in conclusion, that he had broken the experiment tube, heated it, and found under the microscope that it was full of bubbles of gas that had been caught in their passage through the tube.

A Momentous Paper.

Prof. Smithells opened the discussion by saying that he was somewhat breathless at the papers they had heard. It required a great deal of courage for scientific workers to bring forward such results, and they must admire it. Their courage, he thought, was justified, for their experimental record was such as to justify what in others would have been extremely rash. He paid a generous tribute to the care and patience with which Mr. Patterson had conducted the experiments in his laboratory at Leeds. Of the work of Professor Collie and Sir William Ramsay it was unnecessary to say anything. For dramatic interest, he thought, the paper had never been surpassed. The obvious criticism was that in the work enormous weight had necessarily been laid on spectroscopic evidence, and his limited experience in this connection had taught him caution, but he felt sure that the authors were too experienced to fall into such pitfalls.

Sir William Ramsay expressed his great gratification at other researchers having taken up the investigation. With radium there had been no chance of repetition, but the present experiments on transmutation could be reproduced by anyone with a coil and a battery. He was extremely gratified that the theory of transmutation now no longer rested on his *ipsissma verba*.

Prof. Smithells moved that the thanks of the Society be given to the authors, to whom they felt a great obligation, for their momentous communication.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, January 30th, 1913.

Sir Archibald Geikie, K.C.B., President, in the Chair.

Papers were read as follows :—

"*On the Formation of Usually Convergent Fourier Series.*" By Prof. W. H. Young, F.R.S.

"*On the General Theory of Elastic Stability.*" By R. V. Southwell, B.A.

The paper deals principally with the general principles which govern the mathematical investigation of problems in elastic stability, but two examples of some importance are considered for purposes of illustration, viz., the problems of the boiler flue and of the tubular strut.

The boiler flue problem has attracted considerable interest since the publication, by the Royal Society, of Fairbairn's experiments. A thin cylindrical tube, subjected to hydrostatic pressure on its outer surface, may, under certain conditions, be in a state of unstable equilibrium. A formula for the pressure which will produce this state of instability, in a tube of infinite length, has been propounded by Prof. Bryan and others, but doubts have been expressed by Mr. Basset in regard to its accuracy. The investigation of the present paper supports this formula, and leads further to an expression for the strength of a tube of finite length.

The problem of the tubular strut has been discussed by Mr. Mallock. The well-known formula of Euler for the strength of struts is not applicable in the case of thin tubular sections, where failure occurs by wrinkling of the tube-wall, and not by flexure of the axis. In this paper an investigation of the former types of failure is given,

and expressions are found for the values of the end-thrust at which collapse may occur.

In the general discussion of elastic stability the points of greatest interest are—

1. The formulation of general equations, by means of which problems in elastic stability may be investigated with the same accuracy as the ordinary problems of mathematical elasticity.

2. A discussion of the effects of the small inaccuracies which are necessarily met with in practice. Emphasis is placed upon the importance of their consideration in applying the results of theory to practical design.

3. The foundations of a theory of instability in cases where instability is preceded by the occurrence of elastic breakdown in the material under consideration. The practical importance of such a theory is pointed out.

"*A Spectro-photometric Comparison of the Emissivity of Solid and Liquid Copper and of Liquid Silver at High Temperatures with that of a Full Radiator.*" By C. M. Stubbs, M.A.

1. The emissivity of solid and liquid copper and of liquid silver at high temperatures, relative to that of a full radiator at the same temperatures, has been measured throughout the visible spectrum.

2. As in the case of gold, the emissivity of copper is discontinuous at the melting-point, the "relative emissivity" curve of the liquid showing no flexure.

3. The curve of "relative emissivity" of solid copper at high temperatures differs considerably from that of absorptivity at low temperatures. It possesses a much less marked flexure in the green, and it is suggested that this is due to the same causes which ultimately bring about the total absence of a marked bend in the curve for the liquid.

4. Contrary to Burgess's results, no appreciable temperature coefficient of "relative emissivity" was found for liquid copper over a range of 100°.

5. The "relative emissivity" of liquid silver is throughout remarkably low, but seems to be somewhat greater than the corresponding values of the absorptivity of solid silver at ordinary temperatures.

6. "Black body" temperatures of solid and liquid copper and of liquid silver at the respective melting-points are calculated.

"*On a New Analytical Expression for the Representation of the Components of the Diurnal Variation of Terrestrial Magnetism.*" By G. W. Walker, M.A.

Attention is directed to the fact that Fourier analysis of the observed diurnal variation of the components of terrestrial magnetic force does not lead to a concise specification of the data. Thus progress towards a knowledge of the physical causes has been limited.

It is suggested that the phenomena are probably purely diurnal, that no physical significance may attach to the 12-hr., 8-hr., &c., terms, but that the facts may be more suitably expressed by a function that recurs only once in twenty four hours.

Many such analytical expressions may be formed, but one comparatively simple form is considered which represents very closely the dominant features of the experimental results obtained at Kew, Potsdam, and Paris.

The form is quite empirical, but a suggestion is made as to the manner in which such a type may arise in consequence of solar action.

"*An Investigation into the Magnetic Behaviour of Iron and some other Metals under the Oscillatory Discharge from a Condenser.*" By Prof. E. W. Marchant.

The method adopted in the investigation was to photograph by a revolving mirror the spark caused by the discharge. In order to check the accuracy of measurement spark photographs were taken of the discharge from an air condenser through an air core inductance. The agreement between calculated and observed frequencies was within 1 per cent. With a glass condenser the capacity measured by the frequency of the discharge through an air core self-induction was less than that obtained by ballistic measurements. When the discharge from these condensers was passed round a coil having a core of fine iron wires, the discharge consisted of a series of oscillations, the time for each oscillation increasing as the discharge died away. The discharge was much more quickly damped when the iron wire core was inserted. From the measurements of the first half oscillations of a number of discharges the "effective permeability" of the iron wire core was calculated, the "effective permeability" being defined as that which the iron would have if it were constant, in order to give an oscillation of the same periodic time as that which was observed. From these results a curve has been drawn giving the relation between magnetising force and "effective permeability." This curve has been employed to determine approximately the resistance of the spark. The method adopted was as follows:—

For any given discharge the current passing during the first half oscillation was estimated; from the "effective permeability" for the second half oscillation, the magnetising force corresponding to it was found from the curve, and hence the current passing. Hence the loss in energy during the first half oscillation was estimated. The losses of energy consist of:—

1. Ohmic loss in the resistance of the wires.
2. Eddy current hysteresis loss in the iron core.
3. Losses due to the resistance of the spark, and possibly due to dielectric hysteresis.

The spark resistance increases with decreasing current through the spark. The values of the magnetising force used vary from 500 to 5000 gauss, and of current in the spark from 100 to 1000 ampères. The permeability of iron when subjected to the magnetising force due to an oscillating discharge is not sensibly different from that found by ballistic tests. The frequencies employed in these experiments varied from 10,000 to 100,000 cycles per second. With cores made of thicker iron wire, it was found that the "effective permeability" was not very different from that obtained with very fine wires. The damping of the discharge was more rapid with the thicker iron wire cores. With cores of solid iron the discharge was reduced to one-half oscillation.

With cores of solid brass or copper the damping was less rapid than with cores of iron. Nickel wire cores produced similar effects to those observed with iron, but of diminished intensity. Some experiments were made in which the coils were wound round a brass tube about 0·5 mm. thick. This tube completely screened off the effect of the iron wire core when it was inserted. Cores made with fine insulated copper wire produced no effect either on the damping or frequency of the discharge.

"*On the Spontaneous Crystallisation and the Melting- and Freezing-point Curves of Two Substances which Form Mixed Crystals and whose Freezing-point Curve Exhibits a Transition Point. Mixtures of* p*-Bromnitrobenzene and* p*-Chlornitrobenzene.*" By Florence Isaac.

The results obtained in this paper may be briefly summarised.

1. *p*-Bromnitrobenzene, *p*-chlornitrobenzene, and their mixtures have been optically examined under the microscope.

2. The freezing- and melting-point curves for these mixtures have been determined. It has been found that these substances form mixed crystals and give curves of Roozeboom's Type IV. The freezing-point curve shows two branches corresponding to two different sorts of mixed crystals and meeting in a transition point at 84·5°, for a mixture containing 27·5 per cent of *p*-bromnitrobenzene and 72·5 per cent of *p*-chlornitrobenzene. The freezing-point curve was found to correspond very nearly to that already obtained by Kremann for these mixtures though Kremann's curve lies somewhat below it. The melting-point curve also shows two branches, corresponding to the two branches of the freezing-point curve,

and on each of these a different kind of mixed crystal is in equilibrium with the liquid. At the temperature marked by the dotted horizontal line, both sorts of mixed crystals may exist together in equilibrium with a liquid containing 27·5 per cent of *p*-bromnitrobenzene. The melting-point curve here obtained differs widely from that obtained by Kremann, a large part of the curve lying considerably below the latter.

3. The supersolubility curve or curve of spontaneous crystallisation has been determined for these mixtures, and it has been found that each mixture possesses a definite temperature of spontaneous crystallisation. This curve lies almost completely between the melting- and freezing-point curves, and, like them, it shows a break in the neighbourhood of the transition point.

CHEMICAL SOCIETY.

Ordinary Meeting, January 23rd, 1913.

Prof. PERCY F. FRANKLAND, LL.D., F.R.S., President, in the Chair.

(Concluded from p. 69).

13. "*Hydroxyquinol-phthalein Anhydride and Hydroxy-quinolbenzein.*" By KEDAR NATH GHOSH and EDWIN ROY WATSON.

From certain theoretical considerations it was argued that gallein, pyrogallol-benzein, and a compound obtained from benzaldehyde and pyrogallol by condensation with hydrochloric acid (K. Hofmann, *Ber.*, 1893, xxvi., 1139) should have valuable dyeing properties. It was found that pyrogallol-benzein has dyeing properties equally as good as those of gallein, but its good properties have probably been overlooked on account of an unfavourable report (Doebner and Forster, *Annalen*, 1890, cclvii., 63). The condensation of benzaldehyde and pyrogallol gives no dyestuff.

Hydroxyquinol-phthalein anhydride, $C_{20}H_{12}O_7$, obtained by condensing hydroxyquinol and phthalic anhydride, separates from alcohol in red crystals; it forms a *tetra-acetyl* derivative, $C_{20}H_8O_3(OAc)_4$, crystallising from benzene in colourless rhombic form, melting at 267°. It dyes mordanted wool scarlet on alum and tin, violet on chrome, and brownish black on iron mordants. The shades are not fast.

Hydroxyquinol-benzein, $C_{38}H_{24}O_{11}$, was produced by condensing hydroxyquinol and benzotrichloride. It is obtained as a dark red amorphous substance by hydrolysing the pure *tetra-acetyl* derivative, $C_{38}H_{20}O_7(OAc)_4$, which separates from benzene in yellow needle-shaped crystals, melting at 235°. Hydroxyquinol-benzein dyes exactly the same shade as the corresponding phthalein anhydride, and the dyeings are also not fast.

14. "2 : 2'-*Ditolyl*-5 : 5'-*dicarboxylic Acid.*" By JAMES KENNER and ERNEST WITHAM.

The *dinitrile*, m. p. 158°, *dimethyl ester*, m. p. 134°, and *diethyl ester*, m. p. 76°, of 2 : 2'-*ditolyl* 5 : 5'-*dicarboxylic acid* were prepared by the action of copper powder on the corresponding derivatives of *o* iodo *p* toluic acid.

Tetramethyl diphenyl-2 : 5 : 2' : 5'-*tetracarboxylate*, m. p. 156°, was obtained in a similar manner from dimethyl iodoterephthalate.

The properties of certain of these compounds differed from those observed by Liebermann in compounds to which he attributed the same constitution, and the conclusion was drawn that the latter derivatives were differently constituted.

15. "*The Carbonylferrocyanides.*" By HERBERT ERNEST WILLIAMS.

The carbonylferrocyanides exist in the mother-liquor resulting from the working up of "cyanogen mud." They can be recovered by precipitating with ferric salts, boiling the precipitate with lime, precipitating the ferrocyanide present as calcium ammonium ferrocyanide, by converting a portion of the liquor into the ammonium salt, mixing with the bulk, and boiling.

The filtrate is boiled with lime to remove the excess of ammonia and the salt allowed to crystallise. The salts of the alkali- and alkaline earth-metals, including lithium and magnesium, are very soluble, and several are deliquescent. The salts of the heavy metals are for the most part insoluble in water; lead, chromic, stannic, and alumina salts produce no precipitate.

The following salts were described: — *Ammonium* salt, $(NH_4)_3Fe(CN)_5CO,3H_2O$; *dimethylaniline* salt, $(C_6H_5{\cdot}NMe_2)_3H_3Fe(CN)_5CO,8H_2O$, sparingly soluble; *diethylaniline* salt, $(C_6H_5{\cdot}NEt_2)_3H_3Fe(CN)_5CO,3H_2O$, sparingly soluble; *barium* salt, $Ba_3[Fe(CN)_5CO]_2,14H_2O$. The *calcium* salt, $Ca_3[Fe(CN)_5CO]_2,8H_2O$, is deliquescent, and forms *double salts*, $CaKFe(CN)_5CO,5H_2O$ and $CaNH_4Fe(CN)_5,CO$. The cobalt salt, $Co_3[Fe(CN)_5CO]_2,18H_2O$, is reddish pink, loses $13H_2O$ at 100°, and turns blue; it also forms the *salt*, $Co_4K[Fe(CN)_5CO]_3,21H_2O$. The *cadmium* salt, $Cd_3[Fe(CN)_5CO]_2,7H_2O$, is white, and becomes anhydrous at 100°; the cupric salt, $Cu_3[Fe(CN)_5CO]_2,14H_2O$, is pale green, and loses $7H_2O$ at 100°; when crystallised from ammonia it gives the *salt*, $Cu_3[Fe(CN)_5CO]_2,3NH_3,9H_2O$, which is olive-green, and also forms the *salt*, $Cu_7K_4[Fe(CN)_5CO]_6,XH_2O$. The *lithium* salt, $Li_3Fe(CN)_5CO,4H_2O$, is deliquescent, and loses $2H_2O$ at 100°. The *magnesium* salt, $Mg_3[Fe(CN)_5CO]_2,16H_2O$, loses $10H_2O$ at 100°; the *manganese* salt, $Mn_3[Fe(CN)_5CO]_2,18H_2O$, is white, loses $15H_2O$ at 100°, and when oxidised with nitric acid forms a dark brown *manganomanganic* salt.

The *nickel* salt, $Ni_3[Fe(CN)_5CO]_2,13H_2O$, is apple-green, loses $6H_2O$ at 100°, and with ammonia gives the pale blue *salt*, $Ni_3[Fe(CN)_5CO]_2,2NH_3,4H_2O$. The *zinc* salt, $Zn_3[Fe(CN)_5CO]_2,7H_2O$, is white, loses $4H_2O$ at 100°, and gives with ammonia the *salt*, $Zn_3[Fe(CN)_5CO]_2,4NH_3,4H_2O$.

16. "*The So-called Disodium Derivative of Diethyl Malonate.*" By ALEXANDER KILLEN MACBETH and ALFRED WALTER STEWART.

In the course of an investigation of the absorption spectra of malonic acid derivatives, the results of which will be published shortly, the authors have been led to examine the spectra of solutions of diethyl malonate and diethyl methylmalonate in the presence of sodium ethoxide; and as the results do not form part of the main work they are now published.

It was for some time assumed that diethyl malonate was capable of forming both a mono- and a di-sodium derivative. The latter substance would have the composition $Na_2C_7H_{10}O_4$; but Vorländer (*Ber.*, 1903, xxxvi., 268) threw considerable doubt on its existence, as molecular weight determinations in boiling alcohol (Vorländer and Schilling, *Ber.*, 1899, xxxii., 1876) showed that it behaved as if it were a mere mixture of the monosodium derivative with sodium ethoxide. Vorländer concluded from an examination of the conductivities of solutions of the free ester, the sodium derivative, and sodium ethoxide, that a true sodium substitution product was present, and not a mere additive compound of one molecule of ester plus one molecule of sodium ethoxide. To this substance he ascribed the formula $CHNa(CO_2Et)_2$, thus representing it as a C-derivative and not an O-derivative. Considerable doubt is thrown on this conclusion by the later work of Haller and Muller (*Comptes Rendus*, 1904, cxxxix., 1180), for by means of the refractometric method they were able to show that malonic derivatives were salts of ψ-acids having the metallic atom attached to a non-carbon atom. On this assumption, the formula of the monosodium derivative of diethyl malonate would be $NaO{\cdot}C(OEt){:}CH{\cdot}CO_2Et$, whilst the disodium derivative would be $NaO{\cdot}C(OEt){:}C{:}C(OEt){\cdot}ONa$. Substances of such structures should differ very considerably from one

another, and it seemed possible that some fresh evidence might be obtained from this point of view with regard to the existence of the supposed disodium derivative.

Diethyl malonate in the presence of excess of sodium ethoxide shows a band in its spectrum which is not found in that of the free ester. The band has its head at oscillation frequency 3900, and occurs in N/1000-ester solution in the presence of N/10-sodium ethoxide. This band might be due to the presence of either mono- or di-sodium derivative. In order to decide between the two, the spectrum of diethyl methylmalonate in the presence of excess of sodium ethoxide was photographed, and it was found that the band observed in this case was exactly similar to the other, although it occurred at a higher concentration (N/100-ester with N/10-sodium ethoxide). Since in diethyl methylmalonate only one displaceable hydrogen atom remains, it seems fair to conclude from the resemblance between the spectra that only one hydrogen atom is displaced by sodium in diethyl malonate; and that even in the presence of excess of sodium ethoxide no disodium derivative is produced.

The reason for the difference in the dilutions at which the heads of the two bands appear may be traced, in part at least, to the fact that although the concentration of sodium ethoxide is the same in both cases, in the solution of diethyl malonate there are two hydrogen atoms capable of being displaced for every one such hydrogen atom in the diethyl methylmalonate solution. Hence the amount of sodium derivative formed will be less in the latter case than in the former.

Log. thicknesses.	Spectrum transmuted to $1/\lambda$.
Diethyl Malonate in the presence of N/10-*Sodium Ethoxide.*	
50	340
40	352
30	363
24	366
23	369—414, 428
22	373 - 400, 430
21	Head of band, 434
20	438
Diethyl Methylmalonate in the presence of N/10-*Sodium Ethoxide.*	
40	344
33	365
32	367—414, 428
31	367—413, 428
30	Head of band, 428
Diethyl Malonate (N/100) *in the presence of* N/1000-*Sodium Ethoxide.*	
49	418
40	444
Diethyl Malonate (N/1000) *in the presence of* N/100-*Sodium Ethoxide.*	
39	363
36	367—414, 434
34	367—414, 442
33	374—400, 444
32	Head of band, 444
Diethyl Methylmalonate (N/100) *in the presence of* N/500-*Sodium Ethoxide.*	
49	367
48	371
47	371
46	423
40	442
Diethyl Methylmalonate (N/1000) *in the presence of* N/50-*Sodium Ethoxide.*	
39	367—413, 427
38	367—413, 427
37	373—400, 428
36	Head of band, 428
30	444

This view is strengthened by the fact that when a series of solutions containing sodium ethoxide and diethyl malonate were examined, the penetration of the band was found to diminish as the quantity of ethoxide was decreased; that is, as the number of collisions between ethoxide and ester molecules was lessened. It seems evident that spectroscopic evidence cannot be brought into agreement with the idea of the existence of a disodium derivative of diethyl malonate.

The accompanying figures give the outlines of the various curves. The dashes indicate the region of the bands, and the figures on the left-hand represent the logarithms of thicknesses of N/100,000-solution.

17. "*αδ-Derivatives of Adipic and β-Methyladipic Acids, and the Preparation of Muconic and β-Methylmuconic Acids.*" By Henry Stephen and Charles Weizmann.

A full description was given of the compounds of which a preliminary account has been published (*Proc.*, 1912, xxviii., 94), and also of the following:—

Methyl αδ-dibromoadipate,—

$$CO_2Me{\cdot}CHBr{\cdot}CH_2{\cdot}CH_2{\cdot}CHBr{\cdot}CO_2Me,$$

crystallises from alcohol in white needles melting at 75°, and distilling at 182°/10 mm. The corresponding *ethyl* ester melts at 65° and distils at 195°/10 mm.

Muconic acid melts and decomposes at 298°. The methyl ester melts at 158°, and distils at 185°/12 mm. The ethyl ester distils at 200°/12 mm.

β-Methylmuconic acid, $CO_2H{\cdot}CH{:}CMe{\cdot}CH{:}CH{\cdot}CO_2H$, is a white crystalline powder melting and decomposing at 235°. The *methyl* ester distils at 145°/9 mm., and the *ethyl* ester at 175°/10 mm.; both are colourless liquids.

18. "*The Measurement of Tryptic Protein Hydrolysis by Determination of the Tyrosine Liberated.*" By Samuel James Manson Auld and Thomas Duncan Mosscrop.

Brown and Millar's method of following tryptic protein hydrolysis cannot be carried out in ordinary protein digests without the use of an external indicator, since the bromination of tyrosine is not momental towards the end of the reaction. Starch and iodine cannot be used to detect the end-point, since the solution is acid. A suitable indicator for small quantities of bromine (in the presence of sodium bromide) is methyl-violet, which shows marked colour changes.

19. "*The Interaction of Iodine and Thiocarbamide.*" By Hugh Marshall.

In the *Trans. Chem. Soc.* for November last there appears a paper by E. A. Werner on "The Interaction of Iodine and Thiocarbamide; the Properties of Formamidine and its Salts," in which the author refers to work done by me in connection with the same subject (*Proc. Royal Soc. Edin.*, 1902, xxiv., 233). The statements regarding my work and views are so inaccurate that I can only assume that they have been based on some abstract of my paper, and not on the paper itself; thus on p. 2167 of Werner's paper it is stated, in reference to my work and earlier work by McGowan:—"Unfortunately both these investigators were misled as regards the true nature of the compound formed, which they considered to be an additive compound, 'dithiocarbamide di-iodide,' $(CSN_2H_4)_2I_2$, the formation of hydriodic acid and the saline character of the substance having escaped their attention."

As my original paper is not readily accessible to chemists generally, it may be permissible to quote the following passages from it, to show how incorrect the above statement is, so far as it regards my views, and to show that much of what is contained in Werner's paper had already been made known.

On p. 236 (*loc cit.*):—"The nature of such a second reaction is suggested by the saline nature of the compound, and the phenomena are explicable on the assumption that in aqueous solution the di-iodide undergoes ionisation, and that the increased ionisation produced by the dilution is the cause of the diminished dissociation. In addition to the first balanced action:—

$$[(CSN_2H_4)_2I_2 \rightleftarrows 2CSN_2H_4 + I_2],$$

we may therefore assume the second one, represented by the equation :—

$$(CSN_2H_4)_2I_2 \rightleftarrows (CSN_2H_4)_2^{\cdot\cdot} + 2I'.$$

"This assumption that the di-iodide and its analogues are true salts is justified by the readiness with which they undergo double decomposition with other salts, as exemplified by the precipitation of the sparingly soluble dinitrate. Further, the aqueous solution of the di-iodide dissolves free iodine, like solutions of metallic iodides ; it precipitates lead iodide and silver iodide from solutions of lead and silver salts; with mercuric chloride it gives a precipitate of mercuric iodide, soluble in excess of the di-iodide."

On p. 238 : —"It will be observed that thiourea is to a certain extent analogous to a metal; a molecule of it corresponds to half an atom of a dyad metal. Like a metal, it unites directly with the halogens to form salts. It can 'reduce' metallic salts from a higher to a lower stage; thus, Rathke (*Ber.*, 1884, xvii., 297) found that it acts upon cupric sulphate to form cuprous sulphate—momentarily—and the sulphate corresponding to the di-iodide, $CuSO_4 + 2CSN_2H_4 = Cu_2SO_4 + (CSN_2H_4)_2SO_4$.

The cuprous sulphate unites w th more thiourea to form a complex compound. Other cupric salts behave in a similar manner.

"When thio-urea is added to a concentrated solution of ammonium persulphate there is a considerable evolution of heat, and, on cooling, the above sulphate separates out, whilst ammonium sulphate remains in solution,—

$$2CSN_2H_4 + (NH_4)_2S_2O_8 = (CSN_2H_4)_2SO_4 + (NH_4)_2SO_4,$$

orresponding to such an action as—

$$Zn + (NH_4)_2S_2O_8 = ZnSO_4 + (NH_4)_2SO_4.$$

"The exact constitution of the class of salts here dealt with does not appear to have been very fully investigated, and in what precedes I have simply adopted the formulæ generally employed. Adopting the imide formula for thiourea, the most plausible assumption is that the salts may be represented by the graphic formula :—

$$\begin{array}{ll} NH_3X & NH_3X \\ | & | \\ HN{:}C{-}S{-}S{-}C{:}NH & \end{array},$$

"The difficulty of satisfactorily investigating this and other points is considerable, owing to the instability of the hydroxide of the corresponding amine base."

In the interval since the publication of my paper I have, in conjunction with Mr. Blackadder, studied these substances further, and the publication of the results has only been delayed in order to allow of completion of certain details. At the Dundee meeting of the British Association I made a short contribution on the subject, especially with regard to analogous compounds containing the group ·S·S·S· in place of ·S·S·.

NOTICES OF BOOKS.

Die Elektrochemische Industrie Frankreichs. ("The Electrochemical Industry of France"). By M. R. Pitaval. Translated into German by Dr. Max Huth. Halle a.d.S.: Wilhelm Knapp. 1912. (9 M.).

This book, which is volume 42 of the Monographien über Angewandte Elektrochemie, describes the state of technical electrochemistry in France as has already been done in previous monographs dealing with Great Britain and Germany. The author lays special stress on the economic aspect of the industry, and shows clearly the important part which has been played by French investigators and inventors in its development. Those branches in which France has been the pioneer, *e.g.*, the use of the electric furnace for the preparation of aluminium, &c., are treated in detail, and the monograph is most systematically and conveniently arranged. There are sections on the alkali chloride industry, calcium carbide, electrometallurgy, to name only a few subjects, and the furnaces which are in use in different parts of France are fully described. The preparation of alloys of iron is included, and the monograph is well-illustrated.

Die Industrie der Steinkohlenteers und des Ammoniaks. "The Coal Tar and Ammonia Industry"). By Dr. G. Lunge and Dr. H. Köhler. Fifth Edition. In two volumes. Braunschweig: Friedrich Vieweg und Sohn. (Vol. I., 29 M.; Vol. II., 15 M.) 1912.

The last edition of this comprehensive work on Coal and Tar and Ammonia, which is well known and highly valued by technical chemists of all nationalities, appeared in 1900, and a revision of it was urgently wanted. In preparing it the authors have collected much fresh material, both purely scientific and technical, from all sources. The by-products of the coal-tar industry are treated in much greater detail than before, their application being only in its infancy at the time of the appearance of the last edition, and recent advances in methods of preparing illuminating gas are also described. Although the authors fully recognise that statistics rapidly get out of date and lose interest they have made them a prominent feature of the fifth as of the fourth edition, and the economic aspect of the industry is fully discussed.

MISCELLANEOUS.

Royal Institution.—The Friday Evening Discourse on February 28th will be delivered by Prof. the Hon. R. J. Strutt on "Active Nitrogen," instead of Mr. C. T. R. Wilson, who will deliver his Discourse on the "Photography of the Paths of Particles Ejected by Atoms" on March 7th.

MEETINGS FOR THE WEEK.

Monday, 17th.—Royal Society of Arts, 8. (Cantor Lecture). "The Art of Miniature Painting," by Cyril Davenport.

Tuesday, 18th.—Royal Institution, 3. "The Heredity of Sex and some Cognate Problems," by Prof W. Bateson, F.R.S.

Wednesday, 19th.—Royal Society of Arts, 8. "The Adulteration of Jam," by Ernest Marriage.

— Microscopical, 8. "Report on the Lenses of the late Joseph Jackson Lister," by E. J. Spitta. Demonstration on the Use of the Centrifuge in Pond-life Work, by D. J. Scourfield. Slides showing the Development of the Fairy Shrimp (*Chirocephalus diaphanus*), by O. L. Curties. Exhibition of Desmids, by Members of the Biological Section.

Thursday, 20th.—Royal Institution, 3. "The Dawn of Empire in Shakespeare's Era," by Sir Sidney Lee, LL.D., &c.

— Royal Society. "Studies on Enzyme Action—XIX., Urease, a Selective Enzyme—II., Observations on Accelerative and Inhibitive Agents," by H. E. Armstrong, M. S. Benjamin, and E. Horton. "Nervous Rhythm arising from Rivalry of Antagonistic Reflexes, Reflex Stepping as Outcome of Double Reciprocal Innervation," by C. S. Sherrington. "Liberation of Ions and the Oxygen Tension of Tissues during Activity," by H. E. Roaf. "Contributions to the Biochemistry of Growth—Glycogen Content of the Liver of Rats bearing Malignant Growths." by W. Cramer and J. Lochhead. "Changes in the Glomeruli and Tubules of the Kidney accompanying Activity," by T. G. Brodie and J. J. Mackenzie.

— Chemical, 8.30. "Mode of Combustion of Carbon," by T. F. E. Rhead and R. V. Wheeler. "Nomenclature of the Rhamnose Group and of other Substances related to the Aldoxes," by H. Marshall. "Some Green Iron-cyanogen Compounds," by H. E. Williams.

Friday, 21st.—Royal Institution, 9. "Horticultural Investigations at the Woburn Experimental Fruit Farm," by S. U. Pickering, F.R.S., &c.

Saturday, 22nd.—Royal Institution, 3. "The Properties and Constitution of the Atom." by Prof. Sir J. J. Thomson, O.M., F.R.S., &c.

THE CHEMICAL NEWS.

Vol. CVII., No. 2778

ESTIMATION OF THE CARBONATES AND HYDRATES OF POTASSIUM AND SODIUM, WHEN TOGETHER IN SOLUTION.

By W. A. BRADBURY and F. OWEN.

The scheming of a method to effect the above estimations arose from having for analysis a "boiler fluid" for the prevention of scale in steam boilers, and may therefore prove interesting to other analysts.

On considering the matter it seemed a necessity that a separation of the hydrates from the carbonates must be effected before the problem could be solved. The only method which seemed to offer any probability of success depended upon the solubility of the hydrates and the insolubility of the carbonates in absolute alcohol, but in attempting to carry out this idea difficulties arose which have so far prevented a successful result.

A solution of the above salts was made up, of which 20 cc. contained—

	Grm.
Caustic potash	0·037
Caustic soda	0·03894
Carbonate potash	0·0332
Carbonate soda	0·0415

On titration with a standard acid (1 cc. = 0·005 NH_3), using as indicators phenolphthalein and methyl orange, the quantity required was :—

	Phenolphthalein (cc.).	Total (cc.).	Methyl-orange (cc.).
Solution	7·75	10·0	2·25
Theory requires ..	7·74	9·94	2·20

Twenty cc. of the solution was evaporated to dryness, and the dried residue treated with absolute alcohol and made up to volume; an aliquot portion titrated. The result did not nearly correspond with the known quantity of acid required for the phenolpthalein test. Apparently during the operations, the solution had carbonated considerably, although it is only a weak solution and the time of operations short.

To ascertain if this is the case an experiment was made of exposing 10 cc. of the solution in an open Erlenmeyer flask for nineteen hours. The acid required was for the—

	Phenolphthalein (cc.).	Total (cc.).	Methyl-orange (cc.).
Original solution ..	3·75	4·95	1·20
Solution in flask ..	2·45	4·95	2·50

Considerable carbonating has occurred by the exposure. To further verify this, 50 cc. of the solution was evaporated in a tall beaker to one-third of its bulk.

	Phenolphthalein (cc.).	Total (cc.).	Methyl-orange cc.).
The original solution	18·65	24·5	5·85
Solution in beaker ..	14·70	24·5	9·80

To overcome this difficulty the solution was evaporated in a distillation flask connected up to a water-jet pump. The evaporation was thus carried on out of contact with air.

	Phenolphthalein (cc.).	Total (cc.).	Methyl-orange (cc).
50 cc. evaporated—			
The original solution	18·6	24·6	6·0
Evaporated	18·5	24·5	6·0
10 cc. evaporated—			
The original solution	3·75	4·95	1·20
Evaporated	3·55	5·10	1·55

It is thus seen that the difficulty due to carbonating during the evaporation to dryness can be overcome by this method. A portion evaporated to dryness by this method was thoroughly dried, whilst the pump was still working, and the dried residue treated with absolute alcohol and boiled for three hours, a reflux condenser being attached to the flask. The condenser was a quarter inch diameter glass tube, fitted with a U-tube at the top and the bend sealed with mercury. The result of the operation was not satisfactory; the residue in the flask contained a large amount of hydrate with the carbonate.

The experiment was repeated on another portion of the solution, but the result was still unsatisfactory. As this method proved so unsatisfactory the problem was attacked from another standpoint.

On titrating the solution with acid, using phenolphthalein and methyl-orange as indicators, the amount of acid required for the hydrates and the carbonates respectively is obtained, but the difficulty consists in apportioning the acid to each of the salts present (NaHO : KHO : Na_2CO_3 : K_2CO_3); and it seems compulsory that the weight of the total carbonates or total hydrates must be known before this can be done; but by the following method of calculation the difficulty is overcome.

A measured volume of the solution is titrated, using phenolphthalein as indicator. The acid used is equivalent to all the hydrate and half the carbonate; methyl-orange is now added and the titration completed; the additional amount of acid used is equivalent to half the carbonate, therefore the amount of acid required for the carbonates and for the hydrates can be calculated from these figures.

The fully neutralised solution is evaporated to dryness and the residue weighed. The result is the weight of the mixed sulphates, due to the carbonates and hydrates of potassium and soda in the solution.

Calculate the total acid required to its equivalent of potassium sulphate, subtract from this result the weight of the mixed sulphates, and the *difference* is due to the sodium sulphate in the mixed sulphates, owing to the difference in the molecular weights of potassium sulphate and sodium sulphate. The whole of the acid used has been calculated to potassium sulphate, and as the acid was neutralised by carbonates and hydrates, it is evident the proportion of the total sulphate, due to carbonates and hydrate, is equivalent to the amount of acid used for each respectively; therefore the proportion of the above obtained *difference* due to the carbonates and hydrates respectively is also proportional to the amount of acid used for each.

An example, fully worked out, will best show the application of these statements and prove the accuracy of the method.

A solution of the mixed carbonates and hydrates of potassium and sodium required :—

(40 cc. NaHO : 40 cc. KHO) 80 cc. of acid to neutralise the hydrates

(10 cc. Na_2CO_3 : 10 cc. K_2CO_3) 20 cc. of acid to neutralise the carbonates

100 cc. total acid required to neutralise the solution.

	Grm.
Total acid 100 cc. calculated to potassium sulphate	= 0·87
The neutralised solution evaporated to dryness and weighed, *i.e.*, mixed K_2SO_4 and Na_2SO_4	= 0·79
Difference due to Na_2SO_4 in weighed sulphates	= 0·08

(K_2SO_4—Na_2SO_4) : Na_2SO_4 :: D.ff. :
32 : 142 :: 0·08 : 0·355 Na_2SO_4 present in mixed sulphates.

And mixed sulphates 0·79 grm. − 0·355 = 0·435 K_2SO_4 present in mixed ulphates.

Therefore the mixed sulphates consist of.. .. .. { Na_2SO_4 0·355 grm. / K_2SO_4 0·435 „

The proportion of the acid used for the hydrates is 80/100.

The proportion of the acid used for the carbonates is 20/100.

Therefore the proportion of the difference (0·08) due to Na_2SO_4 from the hydrate NaHO is $0·08 \times 80/100 = 0·064$.

Similarly for the carbonates $0·08 \times 20/100 = 0·016$

And by above ratios—

32 : 142 :: 0·064 : 0·284 Na_2SO_4 from NaHO = 40 cc. *n*/10 acid.

32 : 142 :: 0·016 : 0·071 Na_2SO_4 from Na_2CO_3 = 10 cc. acid.

	K_2SO_4.
80 cc. acid used for the hydrates =	0·696
0·284 Na_2SO_4 from the NaHO =	0·348
Difference = K_2SO_4 from KHO =	0·348 = 40 cc. *n*/10 acid
20 cc. acid used for the carbonates =	0·174
0·071 Na_2SO_4 from the Na_2CO_3 =	0·087
Difference = K_2SO_4 from K_2CO_3 =	0·087 = 10 cc. acid.

The figures correspond with the quantities taken :—

80 cc. of acid to neutralise the hydrates.
20 cc. of acid to neutralise the carbonates.

Na_2SO_4 = 0·355	NaHO	0·284 = 40 cc. acid	80 cc.
	Na_2CO_3	0·071 = 10 „	
K_2SO_4 = 0·435	KHO	0·348 = 40 „	20 cc.
	K_2CO_3	0·087 = 10 „	
Totals..	0·790	0·790(*a*) 100	

(*a*) Calculate these sulphates to the corresponding hydrates and carbonates.

EFFLORESCENCE OF CRYSTALS UNDER WATER.

By M FORT, M Sc. (Bradford Technical College).

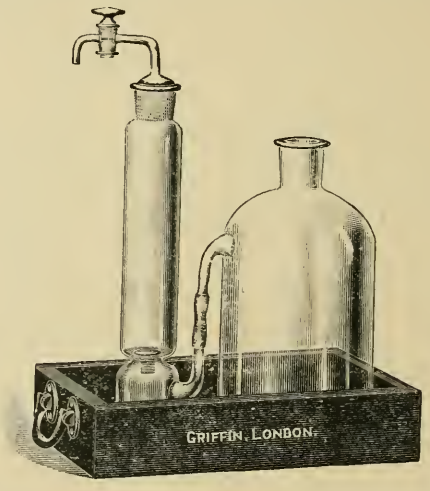
I RECENTLY noticed a curious and, to me, a unique case of crystals losing water of crystallisation in presence of an excess of water. Ordinary sodium sulphite crystals, $Na_2SO_3.7H_2O$, effloresce on keeping, but if the effloresced crystals be taken and placed in an excess of water in a test-tube the opaque outer crust dissolves and the crystals become clean and bright. However, on heating the tube gently the crystals rapidly become opaque and powdered in appearance, as though they had effloresced. That this is actually the case was proved by rapid filtration and air-drying of the clean bright crystals and the effloresced crystals obtained as described. The water contained in each was then estimated gravimetrically. The bright crystals contained an amount of combined water very near that required by the formula $Na_2SO_3.7H_2O$, while the same after heating for a minute under water had lost approximately one quarter of the water of crystallisation. Anhydrous sodium sulphite, of course, can be obtained by heating a saturated solution of the salt, but here there are different conditions; *i.e.*, an excess of water present and the salt already combined with water of crystallisation.

Two explanations offer themselves; firstly, that local saturation causes a deposition of anhydrous salt on the crystals during heating, this deposit being formed from salt which has temporarily been in solution; or, secondly, that dehydration of the crystals, due to rise in temperature, takes place faster than solution can be effected. This latter explanation is the most probable, and is supported by the fact of the rapidity with which efflorescence takes place in air when the temperature is gently raised. The experiment is simple and well adapted for lecture purposes.

GAS GENERATOR.

By F. SOUTHERDEN, B.Sc., F.I.C.

THE apparatus, which has been designed more especially for the generation of hydrogen sulphide for general laboratory purposes, consists of a reaction tower and acid reservoir, connected by a stout rubber union, as shown in the illustration, the lower part of the tower being separated by a radially grooved plug and constituting a drainage chamber. The mode of action is apparent from the figure. Amongst other advantages claimed for the apparatus is the fact that, except for the rubber union, it is made wholly of glass, and for ordinary qualitative analysis the gas requires



no washing, since the upper part of the tower, owing to its height, serves to arrest spray produced below; moreover, the dense stale liquor tends to sink in the reservoir as returned, relatively fresh acid being available on re-starting. A charge consists of about 2 lbs. of iron sulphide and half-a-gallon of acid (suitably a mixture of commercial hydrochloric acid and water in equal volumes), and, when once charged, no further attention is required until the acid is exhausted.

The apparatus is manufactured by Messrs. J. J. Griffin and Sons, Ltd., London.

University College, Exeter.

Royal Institution.—On Tuesday next, February 25th, at 3 o'clock, Prof. H. H. Turner begins a course of three Lectures at the Royal Institution on "The Movements of the Stars"; and on Thursday, March 6th, Mr. W. B. Hardy delivers the first of two lectures on "Surface Energy." The Friday Evening Discourse on February 28th will be delivered by Prof. the Hon. R. J. Strutt on "Active Nitrogen"; and on March 7th, by Mr. C. T. R. Wilson, on "The Photography of the Paths of Particles Ejected from Atoms."

ON THE DENSITY OF SOLID SUBSTANCES, WITH ESPECIAL REFERENCE TO PERMANENT CHANGES PRODUCED BY HIGH PRESSURES.*

By JOHN JOHNSTON and L. H. ADAMS.

(Concluded from p. 78).

The Permanent Effect of Pressure on the Density of Metals.

That pressure may cause a *decrease* in the density of most metals has been known now for some time, though this phenomenon appears not to have attracted as much attention as it deserves in view of its bearing on the question of the constitution of metals. It was first shown for a number of metals by Kahlbaum, though it had been observed in isolated instances several times previous to him, but had not evoked much comment. H. Rose (*Pogg. Ann.*, 1848, lxxiii., 1), observed that hammering silver caused a diminution in its density. Marchand and Scheerer found that pressed copper was, except for cast copper, the lightest, and further, that the density of bismuth decreased after compression (Erdmann, *Journ. Prakt. Chem.*, 1842, xxvii., 209). Several investigators (see F. Reich, *Pogg. Ann.*, cxix., 541) of the density of lead, who obtained results in part discordant, agree that its density is lessened by hammering and drawing, and sometimes by pressure. In 1862, C. O'Neil (*Fortschritte der Physik*, xviii., 10) found that sheet copper diminished in density by hammering, but regained the original value on subsequent annealing. Similar observations were made by A. Riche (*Comptes Rendus*, 1869, lxix., 323); by alternately hammering and annealing blocks of steel or bronze, he found that though the hammering usually increased the density, the process of annealing caused a further increase in each case, instead of a decrease as might be expected. The next paper in point of time dealing with this subject is that of Spring (*Bull. Acad. Roy. Belg.*, 1883 [3], vi., 537, to which we are indebted for some of the references above), who determined the densities of seven metals before and after compression, using a method of experiment exactly similar to that described above in the case of the salts. Spring found that the second compression produced only very slight changes—decreases for two metals, lead and zinc, and increases for tin, bismuth, antimony, cadmium, and aluminium. The foregoing isolated instances would of themselves not deserve much confidence were they not confirmed by the very careful and trustworthy work of Kahlbaum and his collaborators (*Verhandl. Naturforsch. Ges. Basel*, 1903, xv., 9; in part in *Zeit. Anorg. Chem.*, 1902, xxix., 197). The latter distilled a number of metals *in vacuo*, subjected them for 11 hours to a pressure of 11,000 atmospheres, determined the densities, and in five cases out of seven subjected the metal for 1 hour to still higher pressures (Pb, Cd, Au to 12,000 atm.; Cu, Ag to 20,000 atm.); the densities were determined before and after each compression, with an uncertainty of probably not more than $\pm$ 0·0001. His results are reproduced in Table VIII.

Table VIII.—*Influence of Pressure on the Density of Metals Distilled in vacuo (Kahlbaum and Collaborators).*

	Original density.	After 11 hours at 11,000 atm.	After 1 hour at higher pressure.		
	d.	*d'.*	*d''.*	*d*−*d'.*	*d'*−*d''.*
Zn.	6·9225	7·1272	—	0·2047	—
Sb.	6·6178	6·6909	—	0·0731	—
Pb.	11·3414	11·3457	11·3298	0·0043	−0·0159
Cd.	8·6482	8·6477	8·6390	−0·0005	−0·0087
Au.	18·8858	19·2653	19·2646	0·3795	−0·0007
Cu.	8·9326	8·9377	8·9317	0·0051	−0·0060
Ag.	10·4923	10·5034	10·4993	0·0111	−0·0041

* From the *Journal of the American Chemical Society*, xxxiv., No. 5.

From this it is evident that the first compression caused an increase, as might be expected, in the densities of all the metals with the exception of cadmium; but that the second application of pressure caused in every case a diminution, which was so great for three of the metals—lead, cadmium, and copper—that the final density is actually lower than that originally observed, before any pressure had been applied.

Kahlbaum investigated very thoroughly the possible experimental errors, but was forced to the conclusion that the above variations represent real changes in the metals. To account for these changes he advances a somewhat fanciful *ad hoc* explanation on the basis of attractive and repulsive forces between the atoms, but makes no attempt to correlate these changes with other simultaneous changes in the metals. For instance, Kahlbaum remarks that his cylinders of metal had lost their polish and had suffered considerable deformation after compression, and especially after the second compression, but he had noticed these facts only incidentally. We now know that the oil (castor oil) used by Kahlbaum must have been nearly, if not altogether, solid at the higher pressures; consequently the metallic cylinder was then subjected to considerable differential compression, instead of to a simple hydrostatic pressure, as Kahlbaum apparently assumes was the case. This fact accounts for the deformations which he observed.

The more recent investigations instituted by Kahlbaum (Kahlbaum and Sturm, *Zeit. Anorg. Chem.*, 1905, xlvi., 217) on the changes in specific gravity of metals produced by deformation and by subsequent annealing confirm his previous results and those of Spring. He drew, or pressed, wires of various metals and alloys, measured their density, annealed them and again measured their density. The densities of wires which had been twisted a large number of times were also determined before and after annealing. A summary of his results is presented in Table IX. It will be noted that densities of the metals in the soft (annealed) state are greater in each case than the densities in the hard (drawn or twisted) state.

It remained for Spring ("The Effect of Compression in Diminishing the Density of Certain Substances and the Probable Cause of the Phenomenon." *Rec. Trav. Chim. Pays-Bas*, 1904, xxiii., 1; *Journ. Chim. Phys.*, 1903, i., 593) to suggest the most probable explanation for these changes in density: Namely, that a diminution in density occurs only in those cases in which a deformation has taken place. The gist of his argument is briefly as follows: That the substance, while it is being deformed, behaves as if it were partially liquid; that, when deformation has ceased, the substance may not wholly return to its original crystalline state, but partially remains in a state analogous to that of an under-cooled liquid, or, in other words, in an amorphous or glassy condition; and, since the density of the amorphous form is usually less than that of the corresponding crystalline form, the net effect would be a diminution in the observed density. If this reasoning be correct, it follows that metallic bismuth when deformed should show an increase of density, and Spring found this to be so. He fashioned wires of various metals by squeezing the metal through a hole 2 mm. in diameter, and made thin sheets by hammering; the densities were determined, the wires and sheets annealed and the densities again determined, with the following results—

Table X.—*Spring's Results on the Change of Density of Metals Produced by Deformation.*

	Density at 16° of			Mean difference.
	Wire.	Hammered sheet.	Annealed metal.	
Pb ..	11·3351	11·3348	11·3410	−0·0060
Sn ..	7·3011	7·3016	7·3137	−0·0123
Cd ..	8·6558	8·6603	8·6633	−0·005
Ag ..	10·2485	10·2531	10·2696	−0·019
Bi ..	9·8522	—	9·8354	+0·0168

TABLE IX.—*Kahlbaum's Results on the Densities of Wires.*

Metal.	Original density of wire.	Density after annealing.	Difference.	Density after twisting.	Density after annealing.	Difference.
Au	19·2506	19·2602	0 0096	19·2220	19·2322	0·0102
Al	2·6995	2 7031	0·0036	—	—	—
Cd	8·6397	8·6434	0·0037	—	—	—
Ni	8·7599	8·8440	0·0841	8·8273	8·8412	0·0139
Cu-Al	8 2237	8·2377	0·0140	—	—	—
Pt Ir	21·4766	21·4938	0·0172	21·3150	21·3309	0·0159
Pt, commercial	21·4170	21·4320	0·0150	21·4112	21·4284	0·0172
Pt, pure	21·4336	21·4403	0·0067	21·3985	21·4319	0·0327
Wood's alloy (*a*)	9·6661	9·6735	0·0074	—	—	—
Alloy IX.(*b*)	9·2837	9·2940	0·0103	—	—	—
Alloy VIII.(*c*)	9·7711	9·8223	0·0512	—	—	—

(*a*) Composition (per cent): Bi, 50; Pb, 25; Cd, 12·5; Sn, 12·5.
(*b*) Composition (per cent): Bi, 47·75; Pb, 18·39; Cd, 13·31; Sn, 20·55.
(*c*) Composition (per cent): Bi, 52; Pb, 32; Sn, 16.

These results are in agreement with those of Kahlbaum, except for the metals tin and bismuth, which the latter did not investigate. The anomalous behaviour of bismuth as compared to that of the other metals is very important if true, since it furnishes strong evidence in support of Spring's theory.

Experiments with Bismuth.

Bismuth Cylinders.—In order to test this alleged behaviour of bismuth, careful measurements were made of the densities of bismuth cylinders; first, after subjection to high pressures, and again after annealing them. The bomb used for these experiments was of "type D" chrome-vanadium steel. The dimensions were:—Outside diameter 60 mm., diameter of bore 12 mm., length 80 mm. Pressure was applied directly to the metal by means of a hardened steel plunger. The whole sat beneath the press, and pressure was applied to the plunger as previously described. The cylinders were turned down to the proper diameter in a lathe; the diameter of cylinders I. and II. was practically the same as that of the hole in the bomb, while the diameter of cylinder III. was 2 mm. less. The latter cylinder, therefore, when subjected to pressure was probably first crushed to some extent and then welded together again at the higher pressures. As will be seen later, the density of this cylinder changed in a direction opposite to that of the other two. The pressure applied to each cylinder was about 15,000 atmospheres. Density was determined by the principle of Archimedes. The suspending wire was of platinum, 0·1 mm. in diameter, and was platinised according to the procedure of Kohlrausch. The cylinders were annealed by heating in a beaker filled with paraffin oil, and then slowly cooled to room temperature. After being wiped free from oil with a cloth, washed with "petroleum ether," and carefully dried, their densities were again determined. The results corrected to vacuum and to 25° follow:—

TABLE XI.—$d_4/25$ *of Metallic Bismuth, under the Conditions Stated.*

	Cylinder I. 33 grms.	Cylinder II. 32 grms.	Cylinder III. 41 grms.
Density after pressing to 15,000 atmospheres	9·8012	9·7886	9·8001
After heating to 200° for one hour	9·8022 9·8020	—	9·7997
After heating to 240° for two hours	9·8028	9·7898	9·7971

Since the act of forming wires from metals deforms them greatly, it was expected that bismuth wire might show a greater density change on annealing than the compressed cylinders. Accordingly a quantity of bismuth wire 1 mm. in diameter was made by pressing it out from a small bomb through a hole of that size. Wire was thereby produced which was initially flexible, but broke upon being bent back and forth three or four times.

Density of Bismuth Wire.—About 20 grms. of this wire were broken up into lengths of 6 or 8 cm., the pieces were bent into a circular shape and tied together with a weighed platinum wire. The density of the bundle of wires was then determined by the principle of Archimedes, special precautions being taken that no air bubbles remained in or on the bundle of wire. To make sure that this was the case, the wire was covered with air-free water in the beaker in which it was to be suspended. The beaker was then placed in a vacuum desiccator and the water caused to boil under reduced pressure for ten to fifteen minutes. Two determinations of the density of the wire gave 9·7693 and 9·7692 corrected to vacuum and to 25°). After annealing at 230° for two hours the density was 9·7767 and 9·7768.

It will be seen that the density change upon annealing either the cylinders or the wire is in the same direction as with other metals, except in the case of cylinder III. The amount of change is small but undoubtedly greater than the error of experiment, which is probably not greater than +0·0005. The increase of density observed with cylinder III. we attribute to the inclusion of air at high pressure during the probable crushing mentioned above. A small amount of air included in this manner, while having little effect on the density after compression, could expand during the process of annealing and thus give rise to the apparent decrease in density. This explanation may also account for the abnormal change in density observed by Spring, if indeed he made his density determinations on bismuth *before and after annealing*. (For a discussion of this ambiguity *cf.* Kahlbaum and Sturm, *Zeit. Anorg. Chem.*, 1905, xlvi., 303).

General Discussion of the Experimental Data.

Supposing these figures for the effect of pressure on the density of metals to be correct—and the magnitude of the differences surely greatly exceeds the probable experimental error—it may now be regarded as proved that deformation of a metal causes a change—usually a decrease—in its density.

Additional evidence in favour of this point of view is afforded by other papers. Gray and Mees (*Phil. Mag.*, 1890, [5], xxix., 355) noticed that when hard drawn iron, brass, German silver, and pianoforte steel wires were stretched with increasing loads, a slight diminution in density set in when the elastic limit was reached. Grunmach (*Ann. Phys*, 1899, lxvii., 227) stretched a bar of Siemens-Martin steel until it ruptured, and afterwards made a series of very careful density determinations throughout the length of the bar; he found that the density of both portions of the bar was constant and unchanged except at the broken ends, at which the density was less by 0·040 and 0·050 respectively.

From the foregoing examples, then, it is evident that deformation of metals is accompanied by a change—practically always a decrease—of density. This explana-

tion conflicts with none of the available trustworthy experimental evidence on the densities of metals,* and, furthermore, it serves to correlate these facts with a number of phenomena observed by Beilby.

(For the present purpose, the best paper is in *Phil. Mag.*, 1904, [6], viii., 258, in which Beilby summarises all his work up to that date. But see also *Proc. Roy. Soc.*, A, lxxii., 218, 226; lxxvi., 462; lxxix., 463. The more important conclusions have been republished as reports, or abstracts, of lectures delivered by Beilby in Chemical News, *British Association Reports*, and elsewhere).

Beilby's argument may be presented in his own words (*Phil. Mag.*, 1904, [6], viii., 261), it being premised that he uses the terms "crystalline" and "amorphous" to denote a homogeneous and a heterogeneous assemblage of molecules respectively :—

"Metals ordinarily occur in two distinct phases; the hardened or amorphous, which will be referred to as the A phase, and the annealed or crystalline, which will be referred to as the C phase. The A phase is transferred into the C phase by the agency of heat, the C phase is transferred into the A phase by mechanically-produced flow. In the transformations A $\rightleftharpoons$ C there are two intermediate mobile phases, M and M'; so that the transformation may be written A $\rightarrow$ M' $\rightarrow$ C and C $\rightarrow$ M $\rightarrow$ A. The argument is based on evidence drawn from :—

1. The distinct mechanical properties of the two phases A and C.

2. The microstructure of these and the evidence which it supplies of the existence of the mobile phases M and M'.

3. The (*a*) optical. (*b*) electrical, (*c*) thermochemical properties of the phases A and C."

Evidence was obtained in favour of these views with the malleable and dutile metals—gold, silver, platinum, copper, and lead—and also with the brittle and crystalline metals—antimony and bismuth—the behaviour of which falls perfectly in line with that of the former; further, with iron and nickel, which, however, possess other properties which occasionally render their behaviour less plain and simple. The evidence presented in the case of silver, which occupies a fairly central position in respect to hardness and tensile strength, is here recapitulated, in order to show its character.

1. The tensile strength of silver may be raised from under 10 tons per square inch to over 20 tons by rolling, hammering, or wire-drawing. A strip of silver may be made quite hard and springy by hammering, but loses all its spring after heating to 260°.

2. "The micro structure of annealed silver, if the metal is in a sufficiently massive form, is always crystalline, and consists of grains built up of lamellæ of similarly oriented units. In attenuated forms, like leaves or thin films, the structure is determined by surface tension, and has none of the characteristics of crystalline aggregation. The micro-structure of hardened silver is vitreous looking on the surface and finely granular immediately below the surface. The forms assumed by surfaces and edges are rounded and smooth, and suggest the flow of a viscous liquid. When the glassy surface is carefully removed by a solvent, the granular structure underneath is more fully disclosed. By further action of the solvent the granular layer may be completely removed, disclosing the crystalline grains of the C phase more or less deformed or broken up. It seems probable that the granules which are thickly distributed through the vitreous layer are produced by the breaking down of the lamellæ and the setting free of the units of which they are built up. The granules and their vitreous matrix always appear at surfaces of flow, the thickness of the layer being determined by the thoroughness of the flow at that particular place" (*loc. cit.*, p. 262).

3. (*a*) In beaten leaves or films, silver in its hardened state is highly reflecting; by heating to 250—300° the leaf or film becomes transparent and loses much of its reflecting quality; but by flowing or burnishing the annealed leaf or film its opacity and reflecting power are restored.

(*b*) The electrical conductivity of a silver wire in the annealed state is 8—10 per cent higher than that of the same wire in the hardened state. A thermo junction composed of a hardened and an annealed wire of silver gave 0·17 microvolt per degree of difference between the hot and cold junctions; at 260° the electromotive force fell to zero, as the hardened wire then passes into the soft condition. Similar observations have been made by other observers, using various metals (Magnus Maclean, *Proc. Roy. Soc.*, London, A, lxiv., 322; lxvi., 165; Spring, *Journ. Chim. Phys.*, 1903. i., 600).

(*c*) Berthelot (*Comptes Rendus*, 1901, cxxxii., 234) found that the heat of solution in mercury of hammered silver was 2·03 cal., as compared with 0·47 cal. for annealed silver and 0·10 cal. for crystals of electrolytic silver.

Thus by collecting the observations on the mechanical, optical, electrical, and electrochemical properties of the hard and soft forms, it is seen that these all, without exception, support the view that there is a well-marked difference between the two states; further, that they group themselves on either side of a transition temperature common to all; we are therefore justified in regarding these forms of a metal as distinct phases. The transformation from soft to hard cannot be brought about by reducing the temperature below the transition point, provided that no strains are set up thereby (Muir found that hardening by quenching results from the overstraining of the successive layers of material in a rod or mass of metal, *Proc. Roy. Soc.*, London, A, lxxi., 89); but it is readily effected by mechanical means; for instance, in even the lightest and finest polishing this transformation or flow takes place to some extent at and very near to the surface. When the metal is subjected to more drastic treatment, such as hammering or pressing, the effects penetrate to a greater and greater depth, and the transformation "takes place at all points where the strain reaches the stage at which mobility of the molecule is induced by the movement of one portion of substance against another. Thus "exceedingly thin layers of the A phase are formed throughout the whole mass of strained metal. Slipping is easy so long as fresh moving surfaces are forthcoming for the supply of the mobile phase; but when all the available crystalline phase has become encased in the unyielding amorphous phase, plasticity *under these particular stresses comes to an end.*"

"In the more easily flowed metals the surface film formed by polishing may vary from 1000—5000 $\mu\mu$ in thickness, while in the less easily flowed metals they may be 500 $\mu\mu$ or less. At surfaces which have moved over each other very slightly, films of only a comparatively few molecules might be formed."

Beilby was unable by any means to destroy all traces of the crystalline phase, even in the thinnest strips of gold or silver foil; indeed, it has not been possible to produce more than a small percentage amount of the amorphous phase. Hence the properties of the latter can only be very imperfectly ascertained. All the evidence, however, tends to show that this amorphous phase is closely analogous to an undercooled melt, *i.e.*, it bears much the same relation to the crystalline metal as a silicate glass bears to the crystalline silicate.

On this view, then, we should expect as one of the results of the deformation, and consequent flow, of metals, a change of density in the same direction as that produced on melting; which agrees with the results actually found with the metals, bismuth excepted. Too much stress must not be laid on this exception, which may after all be only apparent. For though under ordinary conditions

* The density data brought together in tables, *e.g.*, in Landolt-Börnstein-Meyerhoffer, cannot be made use of for such comparisons; the densities must be determined upon the *same* sample (1) when deformed, and (2) after annealing, in order to obviate the effect of accidental circumstances—flaws, &c.—an effect which might easily exceed the effect sought.

melted bismuth is denser than solid bismuth, it by no means follows that the melt produced at the pressures required to cause the metal to flow should be denser than the solid. As an illustration consider the behaviour of water with pressure (Tammann, *Krystallisieren und Schmelzen*, pp. 315; Bridgman, *Proc. Am. Acad.*, 1912, xlvii., 441); at pressures up to about 2200 atmospheres water is in equilibrium with ordinary ice (ice I), and the melting-point decreases with increase of pressure up to that point; but at pressures greater than 2200 atmospheres, the melting curve rises again, and we have the water in equilibrium with other forms of ice, all of which are *denser* than the liquid water.

The plausibility of this view of the decrease of density of metals which have been deformed is increased by certain other considerations, which, however, can only be referred to here. It is shown, namely, in another paper from the Geophysical Laboratory, Carnegie Institution of Washington (now in course of publication; a preliminary note was published in *Journ. Washington Acad. Sci.*, 1911, i., 260) that many of the properties of metals can be simply correlated if we assume that every *permanent* deformation of a crystalline solid is conditioned by, and consequent upon, a *real* melting; the whole of the solid does not, of course, melt, but only those portions of it which at any instant bear the brunt of the strain. On the basis of this assumption—the reasonableness of which is supported by a large variety of observations on the general behaviour of metals—the possibility of accounting for changes of density following deformation is apparent; a plausible account of the mode of occurrence of these changes could easily be given, but at present it seems premature to do so.

Summary.

1. With a new and improved form of pyknometer we have determined the density of salts and other substances with an accuracy of 3 or 4 units in the fourth decimal place, that is, within 0·02 per cent. In many cases, however, such accuracy is unnecessary since the variations of density due to inhomogeneities of the material may be much greater than this.

2. Powdering a crystalline substance does not change its density by an amount which we can detect with certainty, provided that the material is homogeneous and free from cracks and holes; but if the substance is not homogeneous, then, as might be expected, the fine powder is denser than the coarse particles.

3. Neither does very high hydrostatic pressure produce any after-effect on the density of strictly homogeneous crystalline compounds.

4. But if the pressure be not uniform, then the density of a metal which has been subjected to such compression —or has been deformed in any other way—usually increases first (owing presumably to the filling up of pores and cracks) and then decreases, sometimes even so as to reach a final density less than the original value. Subsequent annealing of the specimen causes a renewed increase of density. The direction of the change of density on compressing bismuth is, contrary to Spring's conclusion, the same as that for other metals, namely, a decrease of density following upon deformation. The bearing of these results upon the question of the "flow" of metals is discussed; they are shown to be in harmony with the idea that the "flow"—or indeed any deformation—of a metal is a manifestation of a real melting, produced by the unequal strains set up during the process.

5. Finally, it is important to emphasise the fact that the density of most substances is somewhat variable, owing to a lack of complete homogeneity of the material. In consequence of this, slight changes of density cannot be regarded as good evidence for the occurrence of any transformation or chemical reaction—whether produced by subjecting the system to compression or by other means.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, February 6th, 1913.

Sir Archibald Geikie, K.C.B., President, in the Chair.

Papers were read as follows:—

"*Influence of the Resilience of the Arterial Wall on Blood Pressure and on the Pulse Curve.*" By S. R. Wells and Leonard Hill, F.R.S.

"*Occurrence of a Ganglion in the Human Temporal Bone, not Hitherto Described.*" By A. A. Gray.

"*Action of Adrenin on Veins.*" By J. A. Gunn and F. B. Chavasse.

"*Preliminary Report on the Treatment of Human Trypanosomiasis, and Yaws, with Metallic Antimony.*" By Capt. H. S. Ranken.

The object of this preliminary report is to demonstrate that intravenous injection of metallic antimony in a fine state of division is a therapeutic measure applicable on a large scale to the treatment of human trypanosomiasis.

A considerable number of cases have been treated by this method, and in a further series combined treatment was employed, salvarsan or atoxyl being given in addition to the antimony. As a routine dose, 1 grain of antimony was given in 4 to 6 ounces of physiological salt solution.

Summaries of results of the various series are given. In the great majority of cases treatment brought about considerable improvement, as evidenced by disappearance of trypanosomes from the blood and lymphatic glands, improvement in nutrition, mental state, &c.

It is not yet possible to determine the ultimate results of treatment. The symptoms following treatment are described; in certain individuals a hypersusceptibility exists.

The action of antimony is discussed, reference being made to the exceedingly rapid trypanocidal action and the effect on the leucocytes. This preparation was also used for yaws. Ten cases were treated and all were cured. The usual course of treatment was three or four doses.

"*Further Researches on the Extrusion of Granules by Trypanosomes and on their Further Development.*" By Major W. B. Fry and Capt. H. S. Ranken. With a Note by H. G. Plimmer, F.R.S., on "*A New Method of Blood Fixation.*"

CHEMICAL SOCIETY.

Ordinary Meeting February 6th, 1913.

Prof. A. Smithells, F.R.S., in the Chair.

Messrs. H. E. Annett, M. P. Applebey, E. Jobling, and A. K. Menon were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Edward Cahen, 32, Queen's Road, Bayswater, W.; Alexander Caruth, 101, Singleton Avenue, Prenton, Birkenhead; Harold Edward Pollock Hodsoll, 22, Pembridge Mansions, Bayswater, W.; Douglas Rayment Keller, B.Sc., 48, Weymouth Street, Watford; Arthur George Abraham Miller, B.Sc., 1, Pretoria Terrace, Waltham Cross; Sosale Garalapury Sastry, B.A., Kavitha Vilas, Mysore, India; Thomas Harrison Winstanley, 45, Dicconson Street West, Wigan; Clifton Wyver, 37, Boulton Street, Wolstanton, Stoke-on-Trent.

Of the following papers, those marked * were read;—

*20. "*The Presence of Helium in the Gas from the Interior of an X-Ray Bulb.*" By Sir WILLIAM RAMSAY, K.C.B. (See p. 79).

*21. "*The Presence of Neon in Hydrogen after the Passage of the Electric Discharge through the latter at Low Pressures.*" By JOHN NORMAN COLLIE and HERBERT SUTTON PATTERSON. (See p. 79).

Addendum.—Since this communication was submitted to the Chemical Society some fresh facts have been obtained by one of the authors (J. N. C.). In order to be certain that the neon had not leaked in from the outside air, through the glass, when the glass was under the influence of the cathode discharge, a tube was made in which that end of the apparatus was inside another tube.

The outside tube was then filled, first with neon, and secondly helium, the inner tube containing the hydrogen. In both cases neon was found in the hydrogen as before, and not a trace of helium leaked in.

A final experiment was made with an entirely fresh apparatus, in which the whole inner tube was encased in an outer one. Again, neon was found in the hydrogen that was sparked in the inner tube.

The vacuum in the outer tube was below that of an X-ray bulb, for the spark would not pass through it. It was thought worth while to wash out this outer tube after the experiment with 1 cc. of pure oxygen. The oxygen was then absorbed by charcoal cooled with liquid air, and a residue remained at least fifty times as great as the residue from the gas in the inner tube. It was a mixture of helium and neon, the helium being in excess. This result has been confirmed by the other author (H. S. P.), who has also found that if the outer tube is filled with oxygen under 10 cm. pressure, the residual gas in the outer tube, instead of being mostly helium, is mostly neon.

*22. "*Vaubel's supposed Phenyldi-imine.*" By MARTIN ONSLOW FORSTER and JOHN CHARLES WITHERS.

Proceeding in the manner described by Vaubel (*Ber.*, 1900, xxxiii., 1711) the authors failed to produce phenyldi-imine, obtaining instead a constant boiling mixture of phenylazoimide and aniline. The percentage composition of a mixture, $C_6H_5{\cdot}N_3 + C_6H_5{\cdot}NH_2$, is identical with that of the supposed phenyldi-imine, $C_6H_5{\cdot}N{:}NH$, and the properties ascribed by Vaubel to this individual accord with those of the mixture in question.

*23. "*The Latent Heat of Vapours.*" (Preliminary Note). By MALCOLM PERCIVAL APPLEBEY and DAVID LEONARD CHAPMAN.

On the assumption that the characteristic equation of a liquid and its vapour can be expressed by the equation—

$$p(v - b) = Rt,$$

in which p is the total pressure (the sum of the external and internal pressures), b a function of the temperature only, R the gas constant, and t the absolute temperature, the authors have deduced thermodynamically that the molecular latent heat of a vapour is given by the equation—

$$L = Rt \log_e \frac{v_2 - b}{v_1 - b} + Rt \left(\frac{1}{v_1 - b} - \frac{1}{v_2 - b} \right) t \frac{db}{dt}.$$

L being the molecular latent heat, and v_2 and v_1 the molecular volumes of the liquid and vapour respectively.

With the aid of S. Young's determination of the latent heat of *n*-pentane vapour (*Sci. Proc. Roy. Dubl. Soc.*, 1910, xii., 414) it has been shown that $\frac{db}{dt}$ is probably almost constant between 30° and 180°, and equal to 0·0892. The value of b at the critical-point is a little greater than a third of the critical volume.

In the following table the observed latent heats of *n*-pentane are compared with those calculated from the above formula.

Latent Heats of n-*Pentane between* 30° *and* 190°.

b = 120·30 at the critical-point; $\frac{db}{dt}$ = 0·0892.

Temperature.	L (observed).	L (calculated).
30°	85·76	86·02
40	84·31	83·22
50	82·13	82·03
60	80·07	79·98
70	77·77	77·73
80	75·33	75·34
90	72·73	72·73
100	69·94	69·93
110	67·31	67·16
120	64·48	64·06
130	60·85	60·60
140	56·58	56·57
150	52·39	52·34
160	47·42	47·46
170	42·06	42·09
180	35·01	35·30
190	24·68	24·51
197·15 (critical temp.)	0·0	0·0

The validity of the formula can be tested with the aid of the discovery of J. E. Mills (*Journ. Phys. Chem.*, 1905, ix., 402) that $\frac{dp}{dt} = \frac{2R}{v}$ at the critical point. For, writing the above equation in the form—

$$L = Rt \log_e \left(1 + \frac{v_2 - v_1}{v_1 - b} \right) + R t \frac{v_2 \; v_1}{(v_1 - b)(v_2 - b)} t \frac{db}{dt},$$

it will be seen that at a temperature just below the critical-point, when $v_2 - v_1$ is small, it reduces to—

$$\frac{L}{v_2 - v_1} = R t \left\{ \frac{1}{v_1 - b} + \frac{1}{(v_1 - b)^2} t \frac{db}{dt} \right\},$$

and—

$$\frac{L}{v_2 - v_1} = t \frac{dp}{dt}.$$

$$\therefore \frac{dp}{dt} = R \left\{ \frac{1}{v_1 - b} + \frac{1}{(v_1 - b)^2} t \frac{db}{dt} \right\}.$$

Introducing the values 120·30 and 0·0892 for b and $\frac{db}{dt}$ respectively, and putting v_1 equal to 309·95, the value given by Young for the critical volume, one obtains—

$$\frac{dp}{dt} = 1{\cdot}996 \frac{R}{v_1},$$

and this is in close agreement with the formula discovered by Mills.

This investigation furnishes evidence for the view that b increases at a uniform rate from the absolute zero to the critical-point, and that it does not diminish as Roth found for ethylene (*Ann. Phys. Chem.*, 1880, [3], xi., 1). The discrepancy between Roth's conclusion and the authors' is probably accounted for by the fact that Roth made the same assumption as Van der Waals, namely, that the internal pressure is at all temperatures proportional to the square of the density, whereas the authors' speculations are independent of any assumption as to the value of this magnitude.

It is obvious that, on the assumption that $\frac{db}{dt}$ is constant, values of b can be calculated from Mills's relation and the law of rectilinear diameter quite independently of the latent heats, and that these values can be used to calculate the latent heats.

DISCUSSION.

Mr. MERRIMAN pointed out that Prof. Young's values for the latent heats of vapours could not strictly be called

"observed" values, as they were calculated from the thermodynamical formula—

$$L = (v_1 - v_2) \cdot \frac{T}{J} \cdot \frac{dp}{dt}$$

the quantities v_1, v_2, $\frac{dp}{dt}$ being read from smoothed curves. This fact should be borne in mind when considering the validity of the conclusions drawn by the authors from the comparison of their new expression with Prof. Young's values, as these values must include any assumptions made in deducing the thermodynamical formula.

24. "*Derivatives of* o-*Xylene*." (Preliminary Note). By JOHN LIONEL SIMONSEN.

With the view of devising a new method for the preparation of 3-nitro-*o*-xylene, the author has investigated the nitration of *o*-xylene-4-sulphonic acid. The three isomeric nitro-*o*-xylene-4 sulphonic acids have been isolated, and yield amides melting at 158°, 180°, and 214° respectively.

The acid which yields the amide melting at 158° has been shown to be 4-*nitro*-o-*xylene*-5 *sulphonic acid*. Experiments are in progress with a view to orientating the other two nitro-sulphonic acids.

The sulphonation of *o*-3-xylidine and *o*-4-xylidine is also under investigation.

25. "*The Alkaloids of* Xanthoxylum brachyacanthum." By HOOPER ALBERT DICKINSON JOWETT and FRANK LEE PYMAN.

The bark of *Xanthoxylum brachyacanthum* was shown to contain 0·06 per cent of γ-homochelidonine, and a quaternary base, which was isolated in the form of its chloride, $C_{21}H_{24}O_4NCl,H_2O$, in a yield of 1·85 per cent. The properties of this salt suggested that it was one of the methochlorides of *l*-canadine. A quantity of the latter alkaloid was therefore methylated, and the α- and *β-methochlorides* were separated, when it was found that the former was identical with the salt from *X. brachyacanthum*.

The physiological examination of *l*-canadine α- and β-methochlorides, which was carried out by Dr. P. P. Laidlaw, showed that both possessed a curare-like action, and that the relative activity in this respect was as 1 to 12 on the frog.

26. "*The Absorption Spectra of Simple Aliphatic Substances in Solutions and as Vapours*. Part II. *Unsaturated Aldehydes and Ketones*." By JOHN EDWARD PURVIS and NIAL PATRICK MCCLELAND.

The chief results obtained in the examination of the absorption spectra of certain unsaturated aldehydes and ketones were (1) the considerable number of narrow bands found in the vapours of acrolein and crotonaldehyde, and which are absent from their solutions; and (2) the absence of similar narrow bands from the vapours of other unsaturated aldehydes, ketones, alcohol, and acid, and the close similarity of their specific absorption with those of the solutions. These results were discussed from a consideration of the ethenoid linking and the carboxyl group acting as primary oscillation centres.

27. "*Phytin and Phytic Acid*." (Preliminary Note). By GEORGE CLARKE.

Phytin was extracted from finely ground oil-free seeds of the ordinary Indian field mustards, a mixture of *Brassica juncea* (Hf. and T.) and *Brassica campestris* (Linn.), by 4 per cent acetic acid or 0·2 per cent hydrochloric acid, and separated from the dark brown acid extract by neutralisation with ammonia. The crude substance was purified by further extraction, and precipitation from dilute acetic acid, and finally by extracting with ice-cold 8 per cent acetic acid, from which it separated on boiling as an amorphous white powder, completely re-dissolving if allowed to cool. The yield was 0·3 to 0·4 per cent of the seeds.

The phytin thus prepared resembled in properties the substance described by Schulze and Winterstein (*Zeit. Phys. Chem.*, 1896, xxii., 90). It was completely soluble in cold, very sparingly so in hot, dilute acetic acid. It was decomposed by heating under pressure at 130—150° with 30 per cent sulphuric acid into phosphoric acid and inositol (hexa-acetyl derivative, m. p. 211°).

The free acid was obtained from the pure phytin described above by precipitating the lead salt from cold dilute acetic acid, decomposing the latter with hydrogen sulphide, and repeating the treatment until the acid residue was completely soluble in 95 per cent ethyl alcohol. This substance consisted of a mixture of approximately equal proportions of phosphoric acid and an acid corresponding with the formula $C_3H_4O(HPO_4)$.

The strychnine salt of the above acid, corresponding with the empirical formula, $C_{24}H_{27}O_7N_2P,2H_2O$ or $C_3H_4O(HPO_4),C_{21}H_{22}O_2N_2,2H_2O$, crystallised from boiling water, in which it was sparingly soluble, in long needles melting and decomposing at 202—203° (uncorr.). It was very easily separated in a pure condition from strychnine dihydrogen phosphate [m. p. 252—253° (uncorr.)], with which it was mixed, by fractional crystallisation from water, the latter salt being very readily soluble in the cold.

28. "*The Constituents of the Oil of* Cydnus indicus." By EDWIN ROY WATSON.

The strong and unpleasant odour of the insect *Cydnus indicus* is due to an oil which it secretes. The oil has been found to contain a large percentage of a non-volatile oil of the same general character as other animal oils. It also contains about 1·5 per cent of an oil which is volatile with steam. This consists of an acid, $C_8H_{14}O_2$, probably *cyclo*-heptanecarboxylic acid, and a small quantity of a non-acid *substance* ($C_{11}H_{20}O_2$?). The acid has a strong rancid odour, and the non-acid volatile substance has a still stronger odour.

29. "*Vapour Density of Ammonium Nitrate*." (Preliminary Note). By PRAFULLA CHANDRA RAY and SARAT CHANDRA JANA.

In continuation of the determination of the vapour density of ammonium nitrite, the authors have extended their work to other decomposable substances under diminished pressure. Ammonium nitrate was selected for the present experiment, and the determination of the vapour density was effected in a modified form of Victor Meyer's apparatus suitable for diminished pressure. It has been found that a part of the salt decomposes into nitrogen monoxide and water, and the rest sublimes. When the tube becomes cold after completion of the experiment, white crystals of the salt were deposited in the neck of the tube. The vapour density was found to be approximately 20. It thus seems probable that the undecomposed part completely dissociates into ammonia and nitric acid in the gaseous state.

30. "*The Solubility of Sulphanilic Acid and its Hydrates*." By JAMES CHARLES PHILIP.

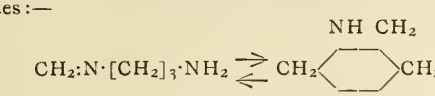
The solubility of sulphanilic acid has been determined at temperatures between 0° and 55°, and the resulting curve exhibits two breaks, corresponding with changes in the character of the solid which is in equilibrium with the saturated solution. The solids which are successively stable in contact with the saturated solution are dihydrate, monohydrate, and anhydrous acid respectively, and the temperatures at which the transitions occur are 21° and 40°.

The dihydrate of sulphanilic acid is an efflorescent substance which loses all its water rapidly and regularly under conditions in which the monohydrate is unchanged, or is dehydrated with extreme slowness. This observation indicates that the water molecules in the dihydrate and in the monohydrate are attached in different ways.

31. "*Hexahydropyrimidine and its Benzoyl Derivatives*." By ARTHUR WALSH TITHERLEY and GERALD EYRE KIRKWOOD BRANCH.

By the action of aqueous formaldehyde on αγ-diaminopropane monohydrochloride, a mixture of the hydrochlorides of methylene-αγ-diaminopropane (I.) and hexahydropyrim-

idine (II.) results, in which the former greatly predominates. On adding alkali the two bases form a tautomeric equilibrium mixture, in which the cyclic form (II.) predominates:—



I. II.

On fractionation the cyclic base distils at about 150°, leaving a polymerised form of the open-chain base, but owing to rapid tautomeric change in the distillate, on refractionation it leaves behind a considerable portion as the non-volatile open-chain base. An aqueous solution of the mixture of bases on titration with acid requires rather more than one equivalent to reach the neutral point, but owing to isomerisation to the cyclic form (and partly to hydrolysis, yielding $\alpha\gamma$-diaminopropane) further gradual addition of acid gives a second neutral point corresponding with two equivalents. Hydrolysis prevents pure crystalline salts being isolated.

The monobenzoyl derivative, $CH_2{:}N{\cdot}[CH_2]_3{\cdot}NHBz$, obtained by the action of formaldehyde on monobenzoyl-$\alpha\gamma$-diaminopropane (*Trans.*, 1912, ci., 2350) is an amorphous ϕ-base of neutral reaction, which with hydrochloric acid rearranges, giving the crystalline hydrochloride of monobenzoylhexahydropyrimidine, but the free base cannot be obtained, since it immediately rearranges to the open-chain amorphous methylene derivative.

1 : 3-*Dibenzoylhexahydropyrimidine* is a stable crystalline solid (m. p. 95°) obtained in quantitative yield by the moist benzoylation of methylene-$\alpha\gamma$ diaminopropane $\rightleftharpoons$ hexahydropyrimidine, and also by the slow action of formaldehyde on dibenzoyl-$\alpha\gamma$-diaminopropane in the presence of concentrated hydrochloric acid.

32. "*Condensation of Ketones with Phenols.*" By Hemendra Kumar Sen-Gupta.

Methyl ethyl ketone condenses with α naphthol in glacial acetic acid solution in the presence of fuming hydrochloric acid, yielding the *anhydride* of 1 : 1-*dihydroxy-methylethyl-* $o\alpha$ *dinaphthylmethane*, $CMeEt<^{C_{10}H_6}_{C_{10}H_6}>O$ (m. p. 154—155°); in common with the members of this type, it crystallises from glacial acetic acid in transparent rhombic plates. A *bromo* derivative melts at 250°, and a *nitro*-compound at 265°. Methyl propyl ketone and diethyl ketone condense under the same conditions, giving respectively the *anhydrides* $CMePr^{\alpha}<^{C_{10}H_6}_{C_{10}H_6}>O$ (m. p. 162°) and $CEt_2<^{C_{10}H_6}_{C_{10}H_6}>O$ (m. p. 166·5°). Acetophenone and α-naphthol, when dissolved in a minimum quantity of glacial acetic acid and saturated with dry hydrogen chloride, condense in the course of five to seven hours at 100°, and the *compound* $CMePh<^{C_{10}H_6}_{C_{10}H_6}>O$ melts at 167°. Benzophenone does not appreciably condense in presence of hydrogen chloride alone; phosphoryl chloride, however, brings about the condensation very readily, and the *compound* $CPh_2<^{C_{10}H_6}_{C_{10}H_6}>O$ melts at 273°. With an excess of the agent, the product is probably identical with that described by Clough (*Trans.*, 1906, lxxxix., 771).

The condensation of acetone and phenol which has been described by Dianin (*Journ. Russ. Phys. Chem Soc.*, 1892, xxiii., 488) requires about twenty-four hours' heating to give a yield of 60 - 65 per cent. It has been found in this connection that by the use of stannic chloride diluted with one and a-half to two times its volume of chloroform, a 50 per cent yield can be obtained in the course of a few hours at 40 — 50°.

33. "*Reaction between Ferric Salts and Thiosulphates.*" By John Theodore Hewitt and Gladys Ruby Mann.

The authors have studied the reduction of solutions of ammonia ferric alum by sodium thiosulphate and of other ferric solutions made up with the alum and potassium thiocyanate, phenol, or acetoacetic ester. The rate at which ammonium ferrisulphate reacts is slower than that shown by ferric chloride; the iron probably forms part of a negative complex.

The reactions measured proved to be all of the fourth order.

(To be continued)

SOCIETY OF CHEMICAL INDUSTRY.
(London Section).

Ordinary Meeting, February 3rd, 1913.

Prof. W. R. Hodgkinson in the Chair.

The following papers were read and discussed:—

"*The Behaviour of Paint under the conditions of Practice, with Special Reference to the Aspersion Cast upon Lead Paints.*" By H. E. Armstrong, F.R.S., and C. A. Klein.

The authors criticise the work of E. C. C. Baly in connection with the alleged toxic effects of white-lead, and maintain that any such effects observed when lead paints are used must be due to volatile products from the turpentine or other thinning material, and not to the lead or oil.

Tests with leaves of *Aucuba japonica* show that blackening of the leaves occurs with paints containing no lead compounds, provided turpentine is present.

Various experiments are described in which the authors were unable to obtain any indication that a volatile compound of lead is evolved from paint.

The work of MM. Breton, Trillat, and others is alluded to, and the authors finally state that "lead paints are to be objected to only on the grounds that they may enter into the system through careless handling or in the form of dust, such as is produced by rubbing down old paint."

"*The Technical Production of Ethane.*" By Colin Sprent.

Ethane was required on account of its low boiling-point (-93° C.) for use in a refrigerating machine, the capacity of which was about 600 kgrms.

After trying all other known methods the author made use of Sabatier's method of "hydrogenation." Ethylene, in the presence of freshly reduced and finely divided nickel, can be made to combine with hydrogen, so that in the equilibrium $C_2H_4 + H_2 \rightleftharpoons C_2H_6$ practically no remainder of either of the gases is left.

The chief difficulties encountered in the investigation to find the proper conditions for this action were, firstly, the production of pure ethylene, and, secondly, the quantitative saturation of this gas with hydrogen. Ethylene was prepared by the method of Mailhe by passing alcohol vapour over alumina, and thereby resolving it into ethylene and water. The optimum temperature for this action appears to be 360° C. Above this point, ethylene begins to decompose, and below it ether is likely to be formed in quantity. Ethylene so prepared needs some purification, or it may impair the catalytic action of the nickel.

The purified ethylene and hydrogen were mixed in equal volumes by aid of the "Rotamesser," and then were passed into the oven containing the nickel. The reaction between ethylene and hydrogen is exothermic, and unless the heat lost by radiation is sufficient, cooling by water-pipes must be adopted. After experimenting in various directions, it was found that combination could be effected quantitatively by passing the first obtained product containing 80 per cent C_2H_6, 10 per cent each C_2H_4 and H_2, at a pressure of 30 to 40 atmospheres, through an iron autoclave filled with nickel pumice.

A trial plant produced 25 kgrms. daily. A large plant is designed to produce 100 kgrms. per diem.

"*The Feeding Value of the Horse Chestnut.*" By S. J. M. AULD.

The horse chestnut (the seed of *Aesculus hippocastanum*) is popularly understood to be poisonous, and has been experimented with as a cattle food only to a very small extent. The whole or the decorticated nut contains a considerable amount of protein and an appreciable percentage of oil.

Feeding experiments were carried out on a calf, a sheep, and two pigs at the Wye College by Mr. G. O. Searle.

The preparation of the nuts by drying, partial crushing, and decortication, and then boiling with water to remove the bitter principle, is described.

It is shown that when prepared horse chestnut was used as part of a mixed feed, a calf increased in weight and improved in condition. The pigs and sheep did not take kindly to the new food.

It appears that when stock can be persuaded to eat it, chestnut meal is a fairly nutritive food, and within the limits of what they will eat not poisonous. Its albuminoid ratio is 1 : 8·6, and the starch equivalent 74.

SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS.

Annual General Meeting, February 5th, 1913.

THE following were elected the Officers and Council for the ensuing year:—

President—Leonard Archbutt.

Past Presidents serving on the Council (limited by the Society's Articles of Association to 8 in number)—Edward J. Bevan, Bernard Dyer, Thomas Fairley, W. W. Fisher, Otto Hehner, R. R. Tatlock, E. W. Voelcker, J. Augustus Voelcker.

Vice-Presidents—George Embrey, J. T. Hewitt, W. H. Willcox.

Hon. Treasurer—Edward Hinks.

Hon. Secretaries—A. Chaston Chapman, P. A. Ellis Richards.

Other Members of Council—R. M. Clark, James Connah, John Evans, George T. Holloway, G. D. Lander, Thomas Macara, G. W. Monier-Williams, Cecil Revis, Harry Silvester, F. Wallis Stoddart, Arnold R. Tankard, John White.

Ordinary Meeting, February 5th, 1913.

Mr. LEONARD ARCHBUTT, President, in the Chair.

MESSRS. Stanley Elliott, Thomas Rigby Greenough, Harold Lowe, James P. Ogilvie, and John Algernon Lacy Sutcliffe were elected Members of the Society.

Certificates were read for the first time in favour of Messrs. Arthur Cecil Bescoby, 24, Saumarez Street, Guernsey, Thomas Walter Firth Clark, 11, Quadrant Road, Canonbury, N.; Frank Edward Day, care of Condensed Milk Company of Ireland, Lansdowne, Limerick; and James Fowler Tocher, County Laboratory, Crown Mansions, 41½, Union Street, Aberdeen.

Certificates were read for the second time in favour of Messrs. John Augustus Goodson, Frederick William Skevington, and John C. White.

Dr. G. T. Beilby was elected an Honorary Member of the Society.

The following papers were read and discussed:—

"*Antipyrine in Toxicological Analysis.*" By G. D. LANDER and H. W. WINTER.

The most suitable methods of extraction and limits of delicacy of recognition of antipyrine in urine and viscera have been determined. Steensma's test—with *p*-diamino. benzaldehyde—is recommended as delicate.

"*A New Method for the Volumetric Estimation of Chromium, Vanadium, and Iron in Presence of One Another.*" By FREDERICK W. ATACK.

The method is based on the oxidation of methylene white (leuco-methylene blue) by chromates, vanadates, and ferric salts, resulting in the production of chromic, vanadyl, and ferrous salts, and of methylene blue, which is then estimated by titration with titanous chloride. Details are given for the estimation of chromium by this method, which does not involve the separation of the metals present.

"*Hardened Oils.*" By ARTHUR W. KNAPP.

The author points out that the solid fats which can now be produced from liquid fats by chemical processes may possibly be used in the manufacture of certain food-stuffs. It is possible, however, that these hardened fats may be injurious to health owing to the presence of small quantities of harmful substances used in the hardening process, and the author calls attention to the necessity for a careful analytical study of these products.

NOTICES OF BOOKS.

The Simple Carbohydrates and the Glucosides. By E. FRANKLAND ARMSTRONG, D.Sc., Ph.D. Second Edition. London, New York, Bombay, and Calcutta: Longmans, Green, and Co. 1912.

THE additions to the second edition of this monograph are of special interest to the botanist and agriculturist. They include a short new chapter on the function of carbohydrates and glucosides in plants, in which the changes accompanying the ripening of fleshy fruits such as the banana are traced, and the significance of glucosides in plant economy and the phenomena of respiration are discussed. More space is given to the detailed description of the natural and synthetic glucosides. As before, glucose is taken as the typical sugar and its constitution, chemical properties, and derivatives are carefully studied in detail, and the other hexoses are then treated less fully, any important points of difference from glucose being pointed out.

Celluloid. By MASSELON, ROBERTS, and CILLARD. Translated from the French by HERBERT H. HODGSON, M.A. (Cantab.), B.Sc. (Lond.), Ph.D. (Heidelberg). London: Charles Griffin and Company, Ltd. 1912.

THIS book may be described as the first complete and practical work on celluloid yet published, and all who are interested in the manufacture or use of this substance will welcome its appearance. Above all the authors have aimed at treating the subject from a most practical point of view, and giving as far as possible actual working details, although they have occasionally found this a matter of some difficulty owing to the jealousy with which manufacturer's secrets are guarded. Theoretical aspects are not by any means neglected, and the theory of nitration, for instance, is discussed at some length. Part I. deals with the general details of manufacture, the colouring and staining of celluloid, for which many recipes are given, the organisation of works, and the analytical methods, including mechanical tests employed in celluloid works laboratories. In Part II. the applications of celluloid are discussed, and some account of substitutes for it is also given, with a brief review of the preparation and properties of the acetates. Throughout the book there are excellent little summaries of the results obtained in investigations and in practice, and attention is frequently drawn to general conclusions.

The Preparation of Organic Compounds. By E. DE BARRY BARNETT, B.Sc. (Lond.), A.I.C. London: J. and A. Churchill. 1912.

THE general methods employed in the preparation of organic compounds are well described in this book, some

by no means common substances being included for description. The author writes perhaps more for works' chemists than for students, and advocates the use of what may be regarded as rather makeshift apparatus, which would possibly be no disadvantage for the technical chemist who has not the very latest laboratory equipment and devices at his disposal. The general theory of the preparation of each group of substances—hydrocarbons, halogen compounds, alcohols, &c., is discussed, and directions are given for the preparation of a great number of substances. These directions, though occasionally rather brief, are usually adequate, and references are frequently given to the original descriptions of the experiments; these are often to be found in German patent literature, which has been thoroughly searched, or in the *Berichte*. Some miscellaneous types of substances, dyestuffs, &c., are included, but, on the other hand, electrolytic methods of preparation are not discussed, and some important classes of substances, such as the sugars, are very scantily treated.

Methods in Chemical Analysis. By Frank Austin Gooch. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1912.

This book contains detailed accounts of the many methods of chemical analysis which have been either originated or developed in the Kent Chemical Laboratory of Yale University, and it lays no claim to be a general text-book of analysis; but it will be found a valuable supplement to such works, and it should find a place in the library attached to every College laboratory. In chapter I. very useful data relating to methods of electrochemical analysis are given. The processes described appear to be rapid, accurate, and easily performed, and the directions are very precise and clear. Some modifications of volumetric methods are also described in chapter I. The individual elements are then considered in turn, both methods of detection and determination being included, and details of the spectroscopic determination of some elements are added. The work of the Kent Laboratory has covered a very wide field, and this summary of the results obtained is of the highest interest to analytical chemists.

Fatty Foods. Their Practical Examination. By E. Richards Bolton, F.C.S., and Cecil Revis. London: J. and A. Churchill. 1913.

The difficult task of the analysis of fatty foods and the identification of fats is well treated in this book, which is full of valuable hints for the comparatively inexperienced analytical chemist. Only the methods which the authors prefer, basing their conclusions upon their long experience of analysis, are given, and this involves the omission of some familiar processes. Thus, for estimating fat in milk only the Gerber and Gottlieb methods are described, the former being recommended as the simplest and quickest process. The authors have devised a good many modifications and simplifications of methods, and their advice concerning the extraction of fats, for instance, will be found valuable and to the point. They impress upon their readers the need for caution in drawing conclusions from experiments. In considering vegetable oils the classification of "Allen's Commercial Organic Analysis" is adopted, and many analyses of feeding cakes are given. The oil fruits are illustrated and described, and complete lists of the characteristics of the oils are included. In the chapter on feeding stuffs the official methods of the Fertilisers and Feeding Stuffs Act are given in full, with the authors' notes and comments on them.

La Grande Industrie des Acides Organiques. ("The Organic Acids Industry"). By Ulysse Roux. Paris: H. Dunod and E. Pinat. 1912.

The author of this book has for many years been engineer-in-charge and manager of factories in which organic acids are made, and the technical world is much indebted to him for placing at its disposal the results of his experience. The substances dealt with include cream of tartar, tartaric acid, and citric acid, and each is treated in much the same way. Thus the properties are first discussed, and statistics and numerical and commercial data are given as fully as possible. The analysis of the raw materials is then described, the process of manufacture is treated in detail, and finally the laboratory control of the large scale process is shortly outlined. In the case of cream of tartar the St. Thibéry method of preparation is described in great detail, many plans, diagrams, and illustrations being inserted. In addition the process which has been worked out by the author, and which has been adopted in Spain, is also fully described, long extracts being given from the patent specification.

CORRESPONDENCE.

THE PERIODIC SYSTEM AND THE RADIO-ELEMENTS.

To the Editor of the Chemical News.

Sir,—I have read with great interest Mr. A. S. Russell's paper on the above subject in the Chemical News of January 31st, 1913.

So far as the chemical properties of the radio-elements have been examined, Mr. Russell's theoretical views agree well with my experimental results. The chemical nature of thorium D has been under examination here since my paper, to be published in the *Journal of the Chemical Society*, was written, and in view of Mr. Russell's contribution it may be of interest to give a preliminary account of the results obtained.

According to Mr. Russell's views thorium D should be analogous either to lead or mercury. Thorium D is certainly not analogous to lead, because on adding lead and precipitating that as chloride, thorium D is left in solution. It is difficult to determine its chemistry owing to its short period, but its volatility is much greater than that of polonium, thorium B, or C, but is less than that of mercury.

It thus appears to be much more nearly allied to the zinc, cadmium, mercury sub-group than to the germanium, tin, lead sub-group. So far, however, it has not been possible to prove that it is completely analogous to any known element.

Alexander Fleck.

University of Glasgow, February 13, 1913.

Protection from X-Rays.—It has long been known that silk can be loaded with various metallic salts, and advantage is taken of the fact in commerce to sell silk which is sometimes weighted with as much as 150 per cent of tin salt. A more legitimate use of this absorptive power of silk is described by Mr. C. Ainsworth Mitchell, in *Knowledge* for February, who says that M. L. Droit has found that by using certain lead salts for the weighting, a silk fabric may be rendered opaque to the passage of X-rays. For example, a material thus prepared by treatment of the silk with lead phosphotannate and other salts contained 68 per cent of mineral matter, including 34 per cent of lead oxide, 24 per cent of tin oxide, 8 per cent of phosphoric anhydride, and 2 per cent of lime and alkalis. Slight discharges of X-rays were practically arrested by two layers of this fabric, while six layers were found a sufficient protection to the skin against the action of an ordinary discharge of medium strength. This fabric had the same protective effect as a sheet of copper 0·044 mm. in thickness, and had the great advantage of flexibility, even when used in a thickness of several layers.

OBITUARY.

MR. GEORGE MATTHEY, F.R.S.

WE much regret to have to announce that Mr. George Matthey, F.R.S., of Cheyne House, Chelsea, died on February 14th in the 88th year of his age.

Mr. Matthey, whose researches in metallurgy were of first-rate importance, became associated nearly seventy years ago with the firm founded by the late Mr. Percival Norton Johnson, F.R.S., and until recently was an active partner in the firm of Johnson, Matthey, and Co., Ltd., assayers and gold refiners, which owed a great debt to his energy and enterprise. Mr. Matthey's scientific work included the investigation of a process for preparing pure platinum from the crude commercial metal by melting it with lead, granulating and dissolving in dilute hydrochloric acid, in which the platinum, iridium, lead, and rhodium are insoluble. The platinum is finally separated off by the action of aqua regia. Another process due to Mr. Matthey is the separation by means of zinc of gold from bismuth-gold alloys, containing only small amounts of the latter metal. He also worked with Deville and Debray on the preparation of pure iridium, which was required for the purpose of making a platinum-iridium alloy to be used for the standard bars for the Parisian Commission of the International Metrical System. This alloy, after series of rigorous tests lasting over a period of two years, was finally pronounced to be the best of all the materials sent in for competition, and all standard weights and measures are now made of it. The firm also manufactures an alloy of 1 part of platinum to 2 parts of silver, which is exceedingly ductile, and is used as a standard of electrical resistance. Comparatively recently they have effected the soldering of platinum apparatus by means of platinum itself, instead of using gold as was formerly done.

Many distinctions were conferred upon Mr. Matthey in recognition of his scientific work. He was elected a Fellow of the Royal Society in 1879, was decorated with the Order of the Legion of Honour and the Austrian Order of Francis Joseph, and received the Prussian Great Gold Medal for Art and Science. He was a Fellow of the Chemical Society, an Associate of the Institution of Civil Engineers, and Vice-President of the Royal Institution in 1896-1897.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xlv., No. 16, 1912.

Transference of Oxygen by Osmium Tetroxide, and Activity of Chlorate Solutions.—K. A. Hofmann. —Osmium tetroxide acts as a slow carrier of atmospheric oxygen. Under ten atmospheres' pressure oxidations are easily effected in presence of OsO_4. Thus a mixture of methyl alcohol and 50 per cent water yields formaldehyde and formic acid. Osmium tetroxide acts only very slowly or not at all on aldehydes. If a piece of paper covered with osmium dioxide hydrate is immersed in a neutral solution of sodium or potassium chlorate, the black colouration disappears, the dioxide being oxidised to tetroxide. This liberation of oxygen by neutral chlorates to osmium dioxide can be used in many oxidation experiments. Thus hydrazine sulphate solution is not oxidised by cold potassium chlorate solution, but if a trace of osmium tetroxide is added, it is oxidised to nitrogen.

Detection of Methane.—O. Hauser and H. Herzfeld. —When ozonised oxygen acts on methane formaldehyde is obtained: $CH_4 + 2O_3 = CH_2O + H_2O + 2O_2$. The reaction occurs at the ordinary temperature, and is complete even when the concentration of the two components is low. Methane is the only hydrocarbon which reacts regularly with ozone to give formaldehyde. With ethane ozone gives acetaldehyde or acetic acid, but much more slowly. With acetylene oxidation to CO_2 occurs with an explosion. The reaction with ozone can be used to detect the presence of methane.

Density of Phosphorus Vapour.—Alfred Stock, George E. Gibson, and Erich Stamm.—The authors have determined the density of phosphorus vapour, using Gibson's membrane manometer. Preliminary experiments showed that under pressures of from 246 to 297 mm. of mercury the density between 500° and 700° corresponded to the molecular weight P_4, and the vapour follows the gas laws. No appreciable dissociation takes place. A complete series of experiments then showed that the dissociation of phosphorus vapour at 1200° under pressures ranging from 175 to 950 mm. of mercury takes place according to the equation of $P_4 \rightleftharpoons 2P_2$.

Hydrogen Borides.—Alfred Stock and Carl Massenez. —The authors have prepared hydrogen borides by the action of hydrochloric acid on magnesium boride. To separate the hydrogen borides from the large excess of hydrogen they used Ramsay and Hatfield's method of cooling with liquid air. They thus found that the essential constituents of the condensate are:—(i.) Hydrogen silicide, SiH_4; (ii.) carbon dioxide; (iii.) hydrogen silicide, Si_2H_6; (iv.) a hydrogen boride, B_4H_{10}, of boiling-point +16°; (v.) a hydrogen boride, B_6H_{12}, boiling at a higher temperature, and having a tension of 10 mm. at 0°; (vi.) a small amount of less volatile residue containing hydrogen borides and silicides, B_4H_{10}, is a colourless liquid or gas with a smell like chocolate. Its melting-point is −112°. It is very unstable, and readily yields a series of fresh borides. The properties of B_6H_{12} are very similar.

Carbon Subsulphide.—Alfred Stock and Paul Praetorius.—Carbon subsulphide, C_3S_2, can be prepared by heating carbon disulphide vapours in a quartz tube at a temperature between 1000° and 1100°. In presence of metals the formation of C_3S_2 begins at a lower temperature. It can also be prepared by passing a current through liquid carbon disulphide, using electrodes of antimony mixed with graphite, the operation being performed in a current of carbon dioxide. Carbon subsulphide is a solid yellowish red substance which, at room temperature, melts to give a red strongly refracting liquid.

MEETINGS FOR THE WEEK.

MONDAY, 24th.—Royal Society of Arts, 8. (Cantor Lecture). "The Art of Miniature Painting," by Cyril Davenport.
TUESDAY, 25th.—Royal Institution, 3. "The Movements of the Stars," by Prof. H. H. Turner, D.Sc., F.R.S.
—— Royal Society of Arts, 4.30. "Openings for Educated Women in Canada," by Miss Ella C. Sykes.
WEDNESDAY, 26th.—Royal Society of Arts, 8. "The Education and Employment of the Blind," by H. J. Wilson.
THURSDAY, 27th.—Royal Institution, 3. "The Dawn of Empire in Shakespeare's Era," by Sir Sidney Lee.
—— Royal Society. "Thermal Properties of Carbonic Acid at Low Temperatures," by C. F. Jenkin and D. R. Pye. "Re-reductions of Dover Tidal Observations, 1883-1884," by E. Roberts.
—— Society of Dyers and Colourists, 8. "Starch and Decomposition Products," by M. Hamburg. "A Method for the Testing of Malt Extracts," by R. J. May. "Valuation of Malt Products," by W. P. Dreaper. "Contribution to the Methods of Testing Malt Extracts," by A. Herz.
FRIDAY, 28th.—Royal Institution, 9. "Active Nitrogen," by Prof. the Hon. R. J. Strutt, F.R.S.
—— Physical Society, 5.
SATURDAY, March 1st.—Royal Institution, 3. "The Properties and Constitution of the Atom." by Prof. Sir J. J. Thomson, O.M., F.R.S., &c.

THE CHEMICAL NEWS.

VOL. CVII., No. 2779.

THE RADIO-ELEMENTS AND THE PERIODIC LAW.

By FREDERICK SODDY, M.A., F.R.S.

IN the paper in which I proved that the two radio-elements, mesothorium I. and radium, are non-separable by chemical processes, and by fractional crystallisation of the chlorides, although the atomic weight of the two e ements differs by about two units, it was pointed out that some of the common elements might also be mixtures of non-separable elements of different atomic weight in constant proportions. In a recent book ("Chemistry of the Radio-elements," p. 30) I stated the rule that held good in several cases, that when the α-particle was expelled the atom passed from a family of even number in the Periodic Table to the next lower-numbered even family, the family of odd number being always missed. Further, in the changes in which the α-particle was not expelled the atom in several cases reverted to its original group, resulting in a curious alternation of properties as the series proceeds. Now, when this occurs, an element of the fourth family, for example, expelling an α-particle and becoming a member of the second family, which after further changes reverts to the fourth family, the two representatives of the fourth family so resulting are not merely similar in chemical properties. They are non-separable by any known process. This applies not merely to the disintegration products of one series but to all the products. Thus, in the fourth group, thorium, uranium X, ionium, radio-thorium, radio-actinium are all chemically non-separable, though they result from three separate series, and the calculated atomic weight varies from 234 to 228.

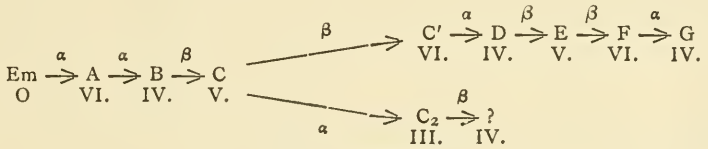
I suggested to my demonstrator, Mr. Alexander Fleck, that he should make a systematic investigation of as many of the radio-elements as possible, the chemical nature of which remained indefinite, and the first part of his results has recently been communicated to the Chemical Society (*Proc. Chem Soc.*, 1913, xxix., 7). As the result of this work at the present time it is possible to state or predict the chemical nature of every known member of the disintegration series, and to bring these series from end to end under a few general laws of the type described, which throw a flood of new light on the nature of the Periodic Law. The lacunæ that still remain to be filled up between uranium and ionium, owing to existence in this part of products with periods of the order of millions of years, can be discussed in a much narrower way in consequence.

In a paper published by A. S. Russell recently (CHEMICAL NEWS, 1913, cvii., 49) some of these generalisations have already been dealt with. Mr. Russell put forward a corollary to my rule for the α-particle which he had previously communicated to me privately in a letter in October, 1912, and which has since been strikingly verified by some of Mr. Fleck's results. Mr. Russell's rule refers to the β-ray and rayless changes, and is that when a β-ray or rayless change occurs the atom changes in chemical nature so as to pass into the family in the Periodic Table next higher in number. That is, the passage in these cases is always from an even to an odd, or from an odd to an even-numbered family. G. von Hevesy (*Phys. Zeit.*, 1913, xiv., 49), who has also been working in Prof. Rutherford's laboratory on the valency of the disintegration products, has put forward very similar views, the difference being that the effect of the β-ray change is considered by him to be the opposite or "polar" to that of the α-ray change, the valency increasing by two after a β-ray change:

The same questions are also very clearly discussed by K. Fajans, who has been connected with the development of our knowledge in the branch series, but his paper did not come to hand until after this paper was drafted (*Phys. Zeit.*, 1913, xiv., 131 and 136). He takes the view here advocated that the Periodic Law is the expression of the periodic character of radio-active changes, and anticipates some of the other points dealt with in this paper.

There is no doubt that Mr. Russell's corollary to my α-ray rule is correct, and I have adopted it just as he has put it forward, but it is possible from Mr. Fleck's results still to learn a good deal that is quite definite as to the nature of radio-active change.

In the first place let us consider the radium series from the emanation to the ultimate product with the branch series that occurs at the C-member. These branch series are now fairly clear owing to the work of Barratt, Marsden, and Darwin in the thorium series, and Makower and Fajans in the radium series, and as I have discussed them fully from the standpoint of the theory of multiple disintegration in the "Annual Report on Radio-activity for 1912" (*Ann. Reports of Progress of Chemistry*, Chemical Society, 1912), I need not further deal with them here.

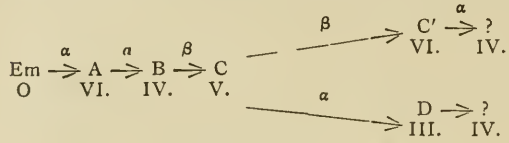


RADIUM SERIES.

Apart from the definite recognition of polonium (RaF) as the homologue of tellurium, and of radium D as non-separable from lead, there was practically nothing known of the chemistry of the other members. From von Lerch's rule and the easy deposition on metals before the phenomenon had been recently investigated from the electrochemical standpoint by v. Hevesy (*Phil. Mag.*, 1912, [6], xxiii., 628) the impression had become general that they might be allied to the noble metals.

From Fleck's results the series runs:—A, unknown; B, lead; C, bismuth; C′, unknown; D, lead; E, bismuth; F, polonium; G, lead. The known members are in accord with the rule about the expulsion of α- and β-particles, and if we extend the rule to the members the chemistry of which is still unknown, it gives for the members of the families of the successive members:—A, VI.; B, IV.; C, V.; C′, VI.; D, IV.; E, V.; F, VI.; G, IV. Now, applying the rule that when similar groups recur the elements are not merely similar, but non-separable, we can predict that in chemical behaviour the two unplaced substances RaA and RaC′ will be non-separable from polonium. The prediction with regard to C′ is unverifiable, as the period of this body is estimated to be only 10^{-6} sec. But with regard to RaA it should be possible to test it, and this is now being done. As regards the branch series, which is difficult to investigate, as only some three out of 10,000 of the atoms choose this route, it may be predicted that RaC_2 is in the third family, and will prove to be non-separable from thallium, as will later be discussed. The end-product of the branch is again lead. The atomic weight of the two end-products, both non-separable from lead, are about 206 and 210 respectively.

In discussing the thorium series similarly, it must be noted that the product termed thorium D is not the analogue of radium D, but of radium C_2, as thorium D is formed from thorium C′, the product giving the longest α-rays, and therefore possessing the shortest life known (estimated at 10^{-11} second).

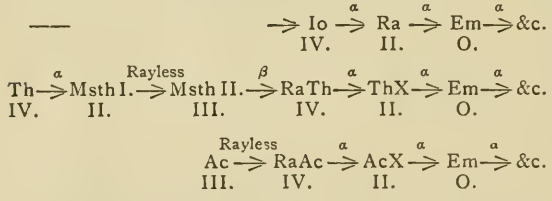


Thorium Series.

It is hardly necessary to discuss it in detail. Thorium A and C′ should be non-separable from polonium, though their periods are too short for this to be determinable. Both end-products, formed in this case in the proportion 65 to 35, should be non-separable from lead, the calculated atomic weight of this "lead" being about 208·5 in each case. ThD, like RaC_2, should prove to be non-separable from thallium.

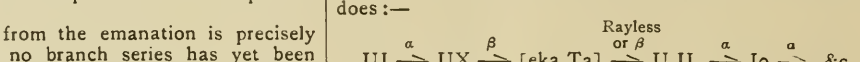
The actinium series from the emanation is precisely analogous, except that no branch series has yet been established. Probably one will be found to exist, but as in radium it may represent an insignificant proportion only of the atoms disintegrating. If actinium is assumed to be analogous to thorium, again both products are non-separable from lead. The main series is analogous to that of thorium and the opposite of that of radium, actinium D being formed in the α-ray change of actinium C.

The series before the emanations furnish also, as Mr. Russell has shown, perfect illustration of the applicability of the rules with regard to α- and β-changes.



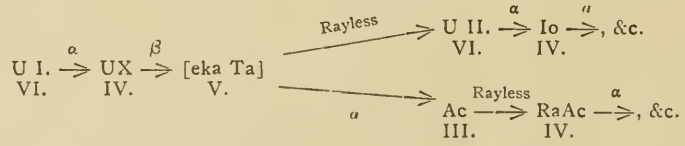
In the thorium series Fleck has shown that mesothorium II., the only member the chemistry of which remained unknown, is non separable from actinium. Mr. Cranston in this laboratory is just completing a research, in which he has proved that radio-thorium is the direct product of mesothorium II., a lacuna that had previously not been filled up, and which is important because the parent of ionium, the product in the uranium series corresponding with radio-thorium in the thorium series, is still experimentally unknown. The actinium series is almost absolutely analogous with the thorium series, actinium itself corresponding with mesothorium II., from which it is non-separable, the only difference being that actinium is rayless like mesothorium I., instead of giving β- and γ rays like mesothorium II. Fleck has shown that radio-actinium, the chemistry of which had remained indefinite, is non-separable from thorium. Russell and Chadwick have described the separation of a body giving α- and β- and γ-rays from radio-actinium, but as radio-actinium is not known to give γ-rays and only gives very soft β-rays, it seems advisable to await further results.

The radium series from ionium onwards is precisely similar to that of thorium from radio-thorium onwards, but lacunæ remain in the connection between ionium and uranium. This part of the table I have been engaged in examining for the last ten years, and my results, though negative for the most part, at least exclude many possibilities. It is clear, as Mr. Russell and several others have pointed out, that uranium X must be the product of uranium I. and not of Uranium II., as hitherto generally assumed. Because the product of uranium I., an α-particle being expelled must belong to the fourth group, and for this to get back to the sixth group at uranium II., two β or rayless changes must ensue. Similarly, the unknown product of uranium X must belong to the fifth group, nowhere else represented, and be the homologue of tantalum. Calling this ekatantalum [eka Ta] it is possible to predict a good deal about its properties from general principles, and the results of my experiments on the product of uranium X (*Phil. Mag.*, 1909, [6], xviii., 858; 1910, xx., 342). It can only give α rays if its period is extraordinarily long. If it does not give α-rays its product must be in the sixth group. So that with fair probability we may write, as Russell does:—



Now, the α-ray producing members all belong to the even families, except in the case of the members where dual disintegration occurs. The C-members, like [eka Ta], belong to the fifth family, and undergo a dual change, such that in one branch a β-ray is followed by an α-ray change, and in the other an α-ray change is followed by a β-ray change. It is scarcely possible to resist the temptation of supposing that such a change is actually going on in [eka Ta], the rayless change into U II., followed by the α-ray change of that substance, in the one branch, proceeding simultaneously with an α-ray change into actinium, which, as is known, changes raylessly, in the other branch.

With regard to the experiments on the product of uranium X in which no growth of α-rays could be detected during the decay of the β-rays, it may be pointed out that a very small growth would be masked by the simultaneous decay of the undeviable β-rays at the same rate. Further, all the products gave α-rays after the β-radiation had disappeared. The first products possessed an activity, which consisted largely of actinium, but in the last products separated, this constituent could only just be detected initially by the active deposit test.



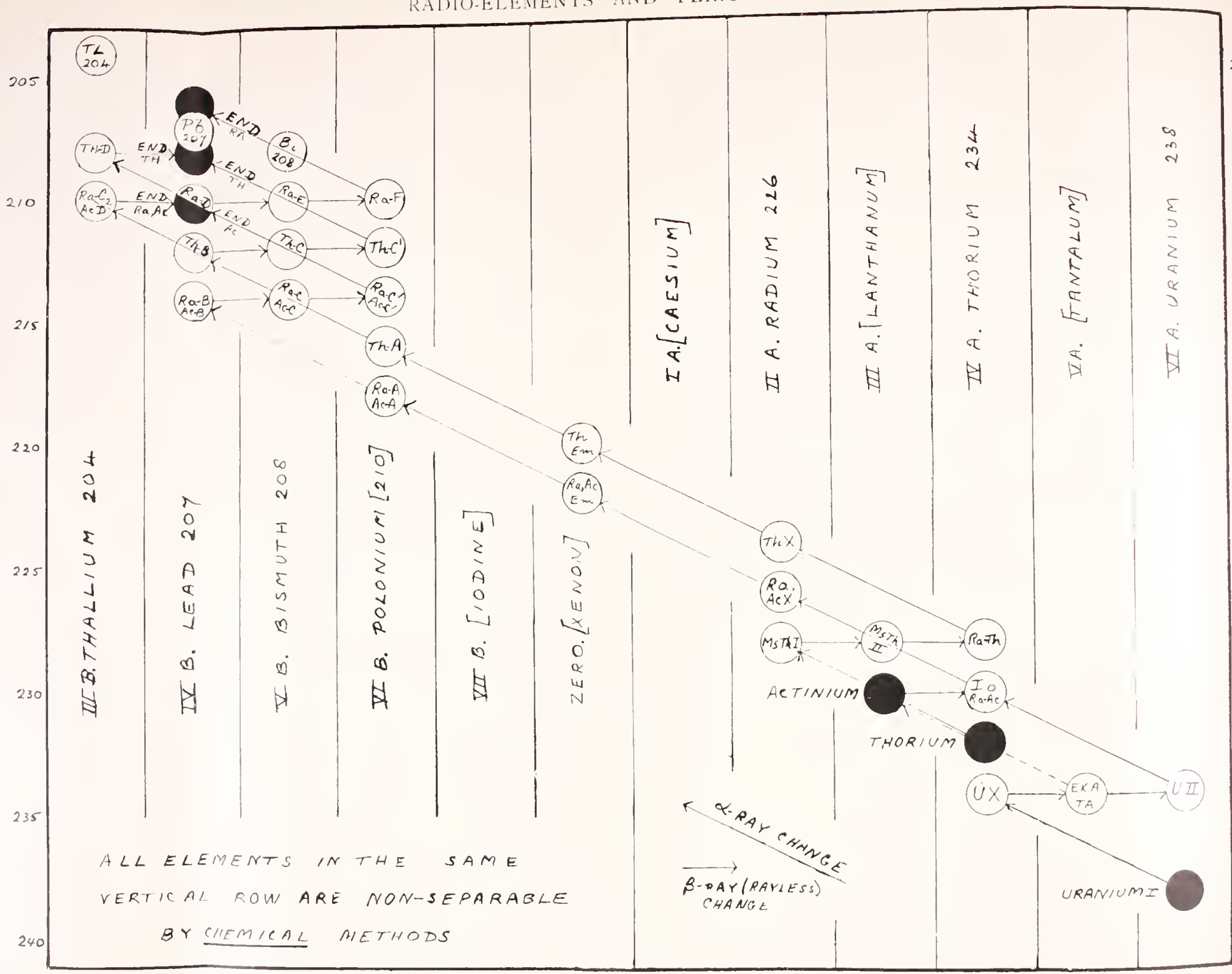
I have some very slight evidence that actinium is really produced from uranium X through an intermediate substance. The actinium present in the last two lots of uranium X preparations, separated from 50 kilogrms. of uranium in June and September, 1909, has been accurately measured over a term of four years, and the measurements reveal an excessively minute but regular growth. In the table the activity of the active deposit produced from the preparations at different times is shown.

	Days from preparation.			
	328.	432.	829.	1281.
Activity (divisions per minute) due to actinium active deposit..	1·43 (?)	1·53	1·70	1·90

The effects are excessively feeble. The conditions of the first measurement were not absolutely comparable with

Th
Em
Ra, Ac
Em
ZERO. [XENON]

RADIO-ELEMENTS AND PERIODIC LAW.



the others, and this is the meaning of the (?). It is clear that much further time must elapse before such measurements can be depended upon for proof of the growth of actinium. If the above scheme is correct it is certain that the period of [eka Ta] must be very long, but as no information exists as to the period of actinium it is impossible to give an estimate. In the meantime the very definite view it is now possible to take of the nature of [eka Ta] should facilitate the search for this missing element, and lead to the problem being more directly elucidated.

Without a single exception, though some cases still remain to be studied, the rule is borne out that all members in all three disintegration series placed in the same family are non-separable from one another. When any place in the Periodic Table was before unoccupied the radio element first discovered to be occupying it appeared as a new type. Thus the homologues of barium and tellurium respectively were unknown before radio-active investigations. Radium and polonium appeared as new types separable from barium and tellurium respectively. But the products radio-thorium, uranium X, ionium, and radio-actinium in the fourth group occupy a place already occupied by the known element thorium, and hence are non-separable from thorium.

This enables it to be predicted that eka tantalum will be separable from tantalum. Actinium also will prove to be separable from lanthanum, as Geisel has stated, but not yet clearly demonstrated.

When the zero group is crossed the place in the sixth family, before occupied by uranium, is now occupied by polonium, in the fifth by bismuth, in the fourth by lead, in the third by thallium. That is, after passing the zero group an entirely fresh set of types is met with, which is shown in the ordinary periodic arrangement by dividing the families into A and B sub-groups. We may predict that the A members and the C′ members of the active deposits will be non-separable from polonium, and that RaC_2 and ThD, possibly AcD, will be not merely analogous to thallium but non-separable from it.

These results prove that almost every vacant place in the Periodic Table between thallium and uranium is crowded with non-separable elements of atomic weight varying over several units, and leads inevitably to the presumption that the same may be true in other parts of the table. As previously pointed out, nothing further is necessary to explain the failure of all attempts to obtain numerical relations between the atomic weights. The view that the atomic mass is a real constant fixing all the chemical and physical properties of the elements is combatted most definitely by the fact that after the α-particle of mass 4 is expelled the members revert later to the original chemical type.

Finally, it may be predicted that *all* the end-products, probably six in number of the three series, with calculated atomic weights varying from 210 to 206, should be non-separable from lead; that is, should be "lead," the element that appears in the International List with the atomic weight 207·1. I should mention that Mr. Russell a year ago told me that he believed that the discrepancy between this value and that calculated (206·0) from the atomic weight of radium by the subtraction of five α-particles was due to the end-product of radium not being lead, but an element non-separable from it. It appears from the foregoing that all the end-products are probably non-separable from lead, and that "lead" is actually such a mixture as formerly, I supposed, might exist among the inactive elements.

If we suppose that all the lead in the world is produced as the end-products in the three disintegration series in constant proportion, the found atomic weight, 207·1, indicates that about half of it may result in that of thorium and the other half in that of uranium. It is, however, hardly profitable to go further in detail until the constancy of the atomic weight of lead from a variety of radio-active minerals has been experimentally tested.

A chart accompanies this paper, showing graphically the evolution of the elements through the Periodic Table from uranium to lead.

Physical Chemistry Laboratory,
Glasgow University, February 18, 1913.

Note added February 22, 1913.—I should have mentioned that if the scheme given is correct and ionium is the direct product of the α-ray change of uranium II.—and it is hardly possible to frame any alternative agreeing with the rules of the α- and β-ray changes laid down—my estimate of the life of ionium as at least 100,000 years (Royal Institute Friday Evening Lecture, March 15th, 1912), becomes definite. It is dependent only upon the absence of long-lived substances, intermediate between these two elements. It follows, therefore, from the experiments of Exner and Haschek, and A. S. Russell and Rossi, discussed fully in my "Annual Report on Radio-activity, 1913" (Section Ionium), in which these investigators failed to observe a single new line in the arc spectrum of ionium thorium preparations, that ionium and thorium must give the same arc spectrum. For on my minimum estimate of the life, the proportion of ionium in the preparations must have been at least 10 per cent by weight. The identity of the spectra of two non-separable elements, although at first sight a somewhat startling deduction, is in agreement with the modern view that the spectrum does not reveal the inner constitution of the atom, as previously assumed, but only its external characteristics. The electrons giving rise to spectra are probably those which condition valency and chemical properties, and are not what have been termed "constitutional electrons." Such "constitutional electrons" are, of course, merely a name for the material atom itself, considered apart from its electronic satellites,

I also take the opportunity of mentioning that Mr. Fleck tells me that he can effect the quantitative separation of thorium D, from the B and C members of the active deposit group, by precipitating potassium in the solution by means of platinic chloride. Taken in conjunction with the other reactions this is in conformity with the prediction that the D members of thorium and actinium will prove to be non-separable from thallium.—F.S.

THE STRUCTURE OF SOME OF THE ELEMENTS.

By HAWKSWORTH COLLINS.

Evidence that the α-particle forms a part of the structure of many of the common elements as well as of the radio-active elements.

In the Chemical News of January 31st (vol. cvii., p. 49) A. S. Russell says that F. Soddy was the first to point out that, after an element had expelled an α-particle, the valency of the resultant product in many cases differed from that of the parent product by two.

This is the first experimental verification of a new chemical law, which was obtained by reasoning upon all experimental data, and inserted in *Nature* as an advertisement (June 14th, 1906), and probably appeared about the same time, also as an advertisement, in the Chemical News and *Knowledge*.

The law was stated as follows:—The acidicity or non-metallic nature of an element is always due to a pair or pairs of electro-positive forces, each pair emanating from a portion of the element, of which the mass is 4, taking the mass of an atom of hydrogen as unity."

This law put into other words is:—"If a certain portion of an element, of mass 4, could be thrown off by any non-metallic element, the valency of the resulting product would be two less than that of the original element."

Sir William Ramsay found that after an α-particle had been given off from radium (at. wt. 226·4) the atomic weight

of the resulting product, niton, is 222·4. Therefore the atomic weight of the α-particle (helium) is 4·00.

In the following investigation this result will first of all be supposed to be correct, and afterwards all experimental results, which can at present be brought into line, will be produced to prove that it is exactly true.

Supposing that an α-particle could be given off from the pentad phosphorus (at. wt. 31·04), a triad should be left of atomic weight 27·04. The triad aluminium has atomic weight 27·1.

Supposing that an α-particle could be given off from the triad aluminium, a monad should be left of atomic weight 23·1. The monad sodium has atomic weight 23·00.

Supposing that an α-particle could be given off from the hexad sulphur (at. wt. 32·07), a tetrad should be left of atomic weight 28·07. The tetrad silicon has atomic weight 28·3.

Supposing that an α-particle could be given off from the tetrad silicon, a dyad should be left of atomic weight 24·3. The dyad magnesium has atomic weight 24·32.

The same may be supposed of the triad boron (11) producing the monad lithium (6·94), the heptad manganese (54·93) producing the pentad vanadium (51·0), the tetrad scandium (44·1) producing the dyad calcium (43·07), and the hexad titanium (48·1) producing the tetrad scandium (44·1).

Two other points to be noticed about these forces are :—

1. That they are quiescent in pairs ; *e.g.*, S can be a hexad, tetrad, or dyad, but never a pentad, or triad, or monad ; P can be a pentad or triad, but not a tetrad, and so on.

2. These pairs of forces always belong to non-metallic elements, and therefore they are said in the law to emanate from those portions of the elements which cause the elements to be classed as non-metallic.

F. Soddy further says that when an α-particle is given off, the resulting product may have two valencies more than the original radio-active element.

This statement may also be illustrated in the case of the simpler elements by noting the valencies and atomic weights of neon, oxygen, and carbon. Neon has no valency, and its atomic weight is 20·2. Oxygen is a dyad with atomic weight 16·0. Carbon is a tetrad with atomic weight 12·0.

Since these are all deductions of the same type, it is evidently correct to take the average difference of these pairs of atomic weights in order to find the atomic weight of the α-particle as follows :—

Difference between Atomic Weights of—		
P and Al		3·94
Al and Na..		4·1
Si and Mg..		3·98
S and Si		3·77
B and Li		4·06
Sc and Ca		4·03
Ti and Sc		4·0
Mn and V		3·93
Ne and O		4·20
O and C		4·00
Ra and Nt..		4·00
	11	44·01
		4·00

Therefore the atomic weight of the the α-particle is 4·00. The atomic weight of helium is 3·99.

The fact that helium has no valency presents no difficulty, for it has been shown that its valencies are frequently self-satisfied or quiescent when it forms part of an element.

It is evident that when it forms part of an element it is mainly connected to the rest of the element by a non-chemically evident force, whilst its two chemical valencies may be quiescent or mutually satisfied, or combined with another pair of chemical valencies in the atom, or they may be active.

It is this non-chemically evident force that has to be overcome before the simpler elements can be disintegrated. And it is evident that for some reason this force becomes weaker as the atomic weight of the element increases.

The above reasoning should be considered together with that which was published in the Chemical News, October 11th, 1907, entitled—"Observations and Deductions obtained from a Consideration of the Numbers given for the Atomic Weights of the Elements by the International Committee (1905) which Lead to a Rational Determination of the Constitution and Structure of each Element."

The following remark by Sir J. J. Thomson in this week's *Nature* has just arrived in time to be inserted here, for a more suitable admission by a well-known scientist could not have been made, even if he had seen the reasoning in this paper. "Sometimes when suffering from the difficulty of clearing out these gases I have been goaded into speculating whether they do not represent the partially abortive attempts of ordinary metals to imitate the behaviour of the radio-active substances, but whereas in these substances the α-particles and the like are emitted with such velocity that they get clear away from the atom, in ordinary metals they have not sufficient energy to get clear, but cling to the outer parts of the atom, and have to be helped by the cathode rays to escape."

The fact that helium can combine with oxygen to form neon has just been shown by experiment. This result was obtained, together with the constitution and structure of nearly all the chemical elements, about nine years ago, and after five or six years had been spent in attempting to get scientists to see the evident truth contained in them, the main deductions were published as advertisements in the Chemical News, March 18th, 24th ; April 1st, 8th, 29th ; May 6th, 13th, 1910. In the number of March 24th the constitution and structure of helium, oxygen, and neon are given, and it will be seen that the constitution of neon is the combination of the constitutions of oxygen and helium. (Explanation given in the number of March 18th).

They were purposely put there to await the time, if it should ever come, when some experimental evidence would confirm any one or more of them.

The results were obtained by reasoning upon all experimental data available, and the majority of them have lately been proved in an entirely different manner by the exact science of mathematics.

NOTE ON THE

DETERMINATION OF ALKALIS IN ROCKS.

By H. V. KRISHNAYYA.

The two methods which are most used for the determina- of alkalis in rocks and minerals are the method of Lawrence Smith (Crookes, "Select Methods in Chemical Analysis," 4th Ed., p. 23), and the hydrofluoric acid method of Berzelius (Treadwell-Hall, "Analytical Chemistry," 2nd Ed., vol. ii., p. 459). Both methods are capable of giving equally accurate results.

Lawrence Smith's method is very neat, and no doubt deserves all the praise that it has received. It is the method that has all along been used in the laboratory of the United States Geological Survey, where so much painstaking and accurate work has been done on the subject of rock analysis, and it has given the Survey chemists every satisfaction. The method, however, necessitates a fusion and subsequent operations for alkalis only, and requires special apparatus. The fusion may be made in an ordinary crucible ; but "the heat has to be kept so low in this case to avoid loss by volatilisation, that perfect decomposition is not always assured" (Hillebrand,

"Analysis of Silicate and Carbonate Rocks," 1910, p. 172). Therefore the special form of crucible and heating apparatus described by Smith are strongly recommended. A somewhat unsatisfactory feature of the method is that it is almost always necessary to apply a correction for the alkali present in the calcium carbonate.

Circumstances may arise where, for want of sufficient material or the special apparatus, it is desired to determine the alkalis in the main solution prepared for the determination of the other constituents of the rock; in such cases the hydrofluoric acid method easily gets the preference. In this method, as usually carried out, the metals of the iron group have to be precipitated twice with ammonia; and if the sample contains at all considerable quantities of these metals, the tediousness of washing the precipitates free of soluble salts is well known to all who have worked this method. If this precipitation with ammonia can be avoided, not only will the time taken for the analysis be considerably shortened, but also the chief trouble in the method will be removed. It has been found that if the constituents of the rock are in solution as sulphates, the iron and alumina can be rendered insoluble, and thus almost completely eliminated at the start by simple ignition.

The method is carried out in the following manner:—About 1 grm. of the material, or a larger quantity if the other constituents besides the alkalis are required to be determined, is decomposed with hydrofluoric acid and excess of sulphuric acid in order to prevent loss of titanium by volatilisation. The sulphuric acid is evaporated off, and the residue boiled with dilute hydrochloric acid. If there is any insoluble residue consisting of undecomposed mineral, it is filtered off and again treated with hydrofluoric and sulphuric acids, dissolved in dilute hydrochloric acid, and this solution added to the main solution. The whole solution is then made up to a definite volume and a portion corresponding to 1 grm. of the mineral is evaporated to dryness in a platinum basin, which is then ignited over a free flame until fumes of sulphuric acid cease to come off. As the alkalis are present as sulphates, no fears need be entertained of their loss by volatilisation. The cake of ignited residue comes away easily from the basin; it is also easily broken up with a glass rod. The residue is transferred to a small beaker, boiled for a minute or two with a little water, and without filtering, precipitated with barium chloride to convert sulphates into chlorides, and then with excess of barium hydrate. From this point the procedure is the same as that usually followed. The barium is completely precipitated with ammonium carbonate. The alkaline chlorides are weighed together, and the potash as chlor-platinate; the amount of soda is obtained by difference.

The two analyses given below indicate the degree of accuracy that may be expected from this method:—

		I. Old precipitation method (per cent).	II. New ignition method (per cent).
(*a*)	Potash	0·52	0·53
	Soda..	3·90	3·88
(*b*)	Potash	0·54	0·55
	Soda..	4·05	4·01

The results given are in each case the averages of two concordant results.

The Lindo-Gladding ("Official Methods of the Association of Official Agricultural Chemists," 1911, p. 11), which is a short method for potash, is intended mainly for fertilisers and other substances which usually do not contain any notable amount of iron and alumina; it does not, moreover, allow of an estimation of soda at the same time. The method of Knop and Hazard (Crookes, "Select Methods in Chemical Analysis," 4th Ed., p. 22), apart from other details, differs from the process described above in not relying upon strong ignition to eliminate iron and alumina.

The Chemical Laboratory, Bangalore,
January, 1913.

THE TRANSPORTATION AND DEPOSITION OF GOLD IN NATURE.

By VICTOR LENHER.

Of all the factors which play an important part in the genesis of ore deposits, the agency of solution is perhaps the most fundamental, for it is by solution that the chemist is able to study and to attempt to imitate the chemistry of ore deposition as carried out in nature. Any information that will throw light on the character of possible ore-bearing solutions may be expected to aid in studying the many problems incident to the solution, transportation, and deposition of the metallic ores.

In connection with some recent chemical studies which have been made with gold, certain solutions have been worked with, the deportment of which toward various reagents as well as with certain minerals, indicates a degree of stability which appears to be of geological significance. Indeed, certain gold solutions possess a stability from the purely chemical standpoint which one would not be likely to expect from our general knowledge of the ease with which gold is deposited out of most of its solutions by even the mildest reducing agents.

How gold is dissolved and transported in underground waters has not been clearly shown. The suggestive work of Stokes (*Economic Geology*, 1906, i., 650) on the solubility of gold in cupric chloride or in ferric chloride solutions at 200° with the re-deposition of metallic gold on cooling, appears to afford a possible means of transportation of gold solutions at elevated temperatures with the subsequent deposition of the gold by lowering of the temperature. The work of Emmons on "The Agency of Manganese in the Superficial Alteration and Secondary Enrichment of Gold-deposits in the United States" (*Trans. Am. Inst. Min. Eng.*, 1910, 767), together with the work of McCaughey (*Journ. Am. Chem. Soc.*, 1909, xxxi., 1263), and Brokaw (*Journ. of Geol.*, 1910, xviii., 321), as well as the earlier work of Pearce (*Trans. Am. Inst. Min. Eng.*, 1893, xxii., 739), Rickard (*Trans. Am. Inst. Min. Eng.*, 1896, xxvi., 978), McIlhiney (*Am. Journ. Sci.*, 1896, 293), and Don (*Trans. Am. Inst. Min. Eng.*, 1897, xxvii., 599), apparently require that free chlorine is the solvent for the gold in the first instance, or if not free chlorine, a solvent whose powers are practically equivalent to that of free chlorine. When the chloride solution of gold is the transporting solution, it seems obvious that the gold is subsequently deposited as metal by a reducing agent. The agency of manganese in the solution of gold and its transportation is consistent in many gold deposits with the accompanying manganese deposits and throws considerable light on the superficial transportation of gold.

The solubility of gold in such media as the alkaline cyanides can hardly be deemed of material importance from the viewpoint of a natural transporting solution. The action of concentrated sulphuric acid or strong phosphoric acid in the presence of oxidising agents on gold will cause solution (Lenher, *Journ. Am. Chem. Soc.*, 1904, xxvi., 550), but this solvent action requires a higher concentration of acid than can be expected in nature. Similarly, though hydrochloric acid under pressure (Lenher, *Econ. Geol.*, 1909, iv., 562) and nitric acid (Dewey, *Journ. Am. Chem. Soc.*, 1910, xxxii., 318) at atmospheric pressure dissolve gold, the solution occurs only in concentrated acids, and the facts are of no importance in seeking for natural solvents for gold.

From all of these acid solutions the precipitation of the gold is usually assumed to take place by ferrous sulphate, metallic sulphides such as pyrites, or, in the case of Stokes's experiments, by lowering of the temperature.

The alkaline solutions which can dissolve and carry gold have not as a rule received as serious consideration as transporting media as the better known chloride solutions. Indeed, the literature on alkaline gold solutions is very

meagre. This is particularly true in regard to the alkaline sulphide solutions.

That gold can be brought into solution by means of the alkaline sulphides has long been known, but it is doubtful if the geological significance of the resulting solutions has been fully appreciated.

Probably at least as early as the time of Glauber it was known that gold can be rendered soluble by fusion with liver of sulphur. Stahl in the seventeenth century ("Observations Chymico-Physica Medicæ") is the first to bring out the fact clearly, and in doing so suggests that Moses burned the golden calf with sulphur and alkali, and gave the solution to the children of Israel to drink.

In more recent times, Skey (*Trans. New Zealand Inst.*, 1872, v., 382), in studying the formation of gold nuggets in drift, suggests the solution of gold in the alkaline sulphides as the medium by which gold can be carried. Eggleston (*Trans. Am. Inst. Min. Eng.*, 1880-1881, ix., 640), in studying the formation of gold nuggets and placer deposits, found spongy gold to be soluble in the alkaline sulphides. Becker (*Am. Journ. Sci.*, 1887, [3], xxxiii., 207), in his studies on the mercury deposits of the Pacific coast, has shown that gold dust dissolves in sodium sulphide. He believed that some of the gold veins bear so considerable a resemblance to the quicksilver deposits, that like the latter they were formed by precipitation from solutions of the soluble double sulphides. Liversidge (*Journal of the Royal Society of New South Wales*, 1893, xxvii., 303), in studying the question of the origin of gold nuggets, reviews the earlier work on the solubility of gold and finds it to be soluble in sodium sulphide.

These solubility experiments have been repeated in our laboratory, and the fact corroborated that metallic gold is soluble in solutions of the alkaline sulphides. More significant, however, appears the fact that from these solutions of gold in the alkaline sulphides, iron pyrites will not throw out the gold.

As is well known, the metals, the metallic sulphides, and even many kinds of organic matter will precipitate gold from the solution of gold chloride. In the case of the alkaline sulphide solutions containing gold, neither pyrites nor metallic iron will precipitate the gold, but on the other hand, gold deposits out of these solutions by exposure of the solution to the air, under which condition the sulphide oxidises.

The sulphide solutions of gold are permanent stable solutions to the ordinary reducing agents; that is to such reducing agents as precipitate gold from the chloride solution. These alkaline sulphide solutions deposit their gold content by contact with acid or by exposure to oxidation. Not only are the alkaline sulphide solutions of gold stable to the metallic sulphides, but experiments made in sealed tubes have demonstrated that sodium, potassium, ammonium, or calcium sulphide solutions will dissolve gold leaf in the presence of pyrites without any deposition whatever of gold on the pyrites.

It is therefore obvious that through the agency of the alkaline sulphides it is possible for gold to be transported in alkaline sulphide solution through a bed of pyrites without deposition of metallic gold, and, indeed, it is possible to think of such a water passing through a bed of gold-bearing pyrites actually enriching itself by solution of the gold from the pyrites. To follow such a solution further, it can be conceived that gold can be carried through a reduced zone, and later the gold can be deposited by meeting acid in the reduced zone, or in absence of acid can be carried indefinitely until it reaches a zone of oxidation when the metal would be deposited.

When sodium thiosulphate is allowed to act on gold in the presence of oxygen, the double thiosulphate of gold and sodium is formed. This double thiosulphate is also formed when auric chloride and sodium thiosulphate are brought together in solution. This salt possesses remarkable stability in that the dilute acids, hydrochloric or sulphuric, do not at once decompose it, nor does ferrous sulphate or oxalic acid, two of the most common precipitating agents for gold, reduce it to metallic gold at once. All of these reagents do in time or in stronger solutions precipitate the gold from this thiosulphate compound. The extraction of metallic gold from silver ores in the thiosulphate extraction process depends on the formation of the double thiosulphate (Stetefeldt, "The Lixiviation of Silver Ores with Hyposulphite Solutions," pp. 15, 38).

These thiosulphate solutions are reasonably stable to iron pyrites, but on standing, metallic gold slowly deposits on the pyrites.

The sulphite solutions of gold are another example of a means in which gold can be held in alkaline solution. Curiously enough the double sulphite of gold and ammonium is quite stable, while the double gold sulphites of the alkalis are not nearly so stable.

Von Haase (*Chem. Zeit.*, 1869, p. 535) has studied the double sulphite of gold and ammonium. Haase worked in ammoniacal solution, and was able to crystallise the double salt out of solution. The ammoniacal solution as prepared by Haase has been made, and has been found to be quite stable to iron pyrites and to metallic iron. Ammoniacal sulphite solutions have been preserved for months in stoppered flasks, and when tested from time to time by withdrawing small portions and acidifying, metallic gold is instantly precipitated. These ammoniacal sulphite solutions when sealed in tubes with iron pyrites or with metallic iron deposited no gold in months.

Both the sodium and potassium gold sulphites have been described by Haase. In solution, these salts are more unstable than the corresponding ammonium compound. The sodium as well as the potassium gold sulphite solutions yield gold to pyrites by a few minutes' contact. In reality a small quantity of the potassium or sodium gold sulphite added to the ammonium gold sulphite solution increases very much the instability of the latter toward reducing agents; indeed, it is only necessary to add a small quantity of the sodium or potassium compound to the ammonium salt to cause the latter to lose its gold to pyrites practically as readily as though no ammonium salt had been present. This tendency on the part of the fixed alkalis to increase the instability of the ammonium gold sulphite solutions would seem to indicate that the sulphite solutions are not so plausible a means of transportation of gold in underground waters, inasmuch as in most natural waters sodium and potassium salts are present, while ammonium salts are found only in traces. Indeed, natural ammoniacal solutions free from the alkalis are quite unknown.

The alkaline solutions of gold in the lower form of valence of gold, namely, the aurous state, present some interesting phenomena when considered from the viewpoint of transportation of gold.

The aurous state of gold is produced when the ordinary or auric salts are reduced in a certain definite manner. The agencies by which this lower state of oxidation of gold can be produced are limited.

Aurous chloride and bromide are produced by the action of a moderate heat on the ordinary auric chloride or bromide. Experiments made recently in the laboratory show that by proper control sulphur dioxide, one of the best laboratory reducing agents and one of the common reagents used to precipitate gold from solution, can be used to effect the reduction of gold from the auric to the aurous state.

When sulphurous acid is added to a neutral or acid solution of gold without having present some other salt, it is very difficult to stop the reduction of the auric form of gold at the aurous state, the tendency being to produce complete reduction with the precipitation of metallic gold. If, however, a large excess of any of the alkaline chlorides, calcium, magnesium, or zinc chlorides, be present, the reduction of the auric form of gold to the aurous state by means of sulphurous acid can be readily controlled. When an ordinary auric chloride solution is treated with a large excess of one of the above mentioned chlorides, and the solution then treated with a solution of sulphurous acid,

the amber-yellow colour of the auric chloride gradually fades until the solution is rendered completely colourless. This colourless stage represents the existence of the aurous form of the gold, and the gold exists in this solution in all probability as a double aurous chloride.

Solutions of gold prepared in the manner indicated are far more stable under certain conditions than the ordinary auric chloride solutions. These conditions in which marked stability has been observed are somewhat curious. When such a solution is kept out of air contact, and when no free acid or at most very little free acid is present, the solutions are fairly stable; if, however, the solution is exposed to the air, gold begins slowly to deposit. As far as the experiments have gone on this line, it seems as though the precipitation of metallic gold from this partially reduced solution when exposed to the air is due to autoreduction to metallic gold by the oxygen of the air.

The partially reduced or aurous solution out of air contact is far more stable to pyrites than the ordinary or auric compounds. Here, again, is a suggestive solution so far as transportation of gold is concerned.

Of the various means of solution and transportation of gold which have been observed, it would appear that the alkaline sulphide solution may with study solve some at least of the problems of gold deposits. At all events, a solution is known which will not lose its gold to pyrites, and yet will transport gold. The alkaline sulphides can easily be conceived as important natural solvents, and while other alkaline solutions such as the aurous solutions possess considerable stability, yet their formation in nature would not appear to be so likely as the sulphide solution. —*Economic Geology*, vii., No. 8.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, February 13th, 1913.

Sir Archibald Geikie, K.C.B., President, in the Chair.

Papers were read as follows:—

"*A Cassegrain Reflector with Corrected Field.*" By Prof. R. A. Sampson, F.R.S.

The purpose of this memoir is to discover an appliance which shall correct in a practical manner the faults of the field of a Cassegrain telescope while leaving unimpaired its characteristic features of great focal length, convenient position of the observer, and achromatism. It is shown in agreement with the investigation of Schwarzschild that two mirrors alone cannot correct the field without introducing impracticable curves or sacrificing the general design. A system of lenses is investigated which shall effect the purpose. Three lenses is the least number which can satisfy the two conditions of achromatism. Achromatism for all colours is preserved completely by making all the lenses of the same glass. The first of these lenses is a meniscus silvered at the back, and besides adjusting the achromatism of the other two, serves to reverse the direction of the ray. The other two form a pair of nearly equal but opposite focal lengths and intercept the out coming beam. By a proper distribution of curvatures between their faces they introduce correcting aberrations. The resulting field is completely corrected for colour, spherical aberration, coma, and curvature of the field. Points on the object are represented by small circles in the image which reach a diameter of about 2″ at 1° from the centre of the field. This is for a great mirror of 40 inches diameter with an effective focal length of 509 inches and a total length of instrument of 167 inches. Distortion is present but would be allowed for by a computed correction to measures made.

All the surfaces are spherical except the great mirror, which is intermediate between the paraboloid and sphere. The curves are all shallow, and the greatest angle which the ray makes with any of the surfaces is 11°.

"*Studies of the Processes Operative in Solutions.* XXV. *The Influence of Non-electrolytes on Solubility. The Nature of the Processes of Dissolution and Precipitation.*" By Prof. H. E. Armstrong, F.R.S., and J. V. Eyre, Ph.D.

"*Studies of the Processes Operative in Solutions.* XXVI. *The Disturbance of the Equilibrium in Solutions of Fructose by Salts and by Non-electrolytes.*" By E. E. Walker.

"*Excitation of γ-Rays by the α-Rays of Ionium and Radiothorium.*" By J. Chadwick and A. S. Russell.

The work on the excitation of γ-rays by α-rays, shown first by Chadwick in the case of the α-rays of radium C, has been extended to ionium. A preparation of ionium and thorium equal in α-ray activity to 3 mgrms. of radium, after purification from all radio active bodies which emit β- and γ-rays, was found to emit a small but easily detectable amount of γ-radiation. This radiation is shown to be excited by the α-rays, either in the ionium itself or in the thorium with which it is mixed. It is a mixture of three types of radiation differing widely in penetrating power. The first of these has a value of absorption coefficient divided by density (μ/D) in aluminium of 400 $(cm.)^{-1}$, the second of about 8·4 $(cm.)^{-1}$, and the third of 0·15 $(cm.)^{-1}$. The energy of the radiation is mainly confined to the softest type. The value of μ/D for the second type is practically identical with that found by Chapman for the characteristic γ-radiation of thorium of series L. These results, in light of Rutherford's theory of the origin of the β- and γ rays of radio-active substances, point to the probability that the three types of radiations are characteristic radiations of ionium of different series. It has been found also that radiothorium emits a small quantity of γ-radiation, but a detailed study of its nature has not been made.

"*Load extension Diagrams taken with the Optical Load-extension Indicator.*" By Prof. W. E. Dalby.

In this paper further experiments with the indicator are described. The optical load-extension Indicator itself was fully described and illustrated in a paper read on March 7th, 1912.

Load extension diagrams obtained from phosphor-bronze, gun-metal, and brass are shown together with micro-photographs taken from the specimens tested. The chemical analyses of the metals are given in each case.

The effect of annealing brass rod is brought out by comparing the load-extension diagrams of an annealed and an unannealed specimen and by making a similar comparison of the corresponding micro-photographs of the structure of the material.

The physical effect of annealing is to produce a state in which the load-extension curve approaches the shape given by copper, and bears little resemblance to the curve obtained from the same material in an unnealed state. The micro-photograph of the annealed specimen shows that the aggregates have increased in size and have become of one kind.

The most striking diagram shown is that taken from a piece of mild steel which was broken by a suddenly-applied load. The specimen and the indicator were placed in series in a 30-ton testing machine, the straining cylinder of which was connected directly to a power main in which the pressure was 1500 pounds per square inch. The valve to the straining cylinder was opened wide as quickly as it could be done. The specimen passed through its elastic period in a fraction of a second and then passed into the plastic period and drew out to the break, the time occupied from start to finish being only ten seconds.

This experiment and others relating to the elastic period are briefly discussed.

CHEMICAL SOCIETY.

Ordinary Meeting February 6th, 1913.

Prof. A. SMITHELLS, F.R.S., in the Chair.

(Concluded from p. 93).

34. "*Influence of Acetylacetone on Ionic Reactions.*" By JOHN THEODORE HEWITT and GLADYS RUBY MANN.

The action of acetylacetone in hindering the precipitation of ferric phosphate from solutions of ammonia iron alum led to a general examination of the action of this substance on solutions of metallic salts, since other metals besides iron furnish volatile acetylacetonates. Approximately N/20-solutions of various metallic salts were prepared, also solutions containing 12·5 and 17·5 grms. of acetylacetone per litre. One volume of salt solution mixed with an equal volume of the solution of the acetylacetone would give a solution in which for 1 atom of metal about 2½ molecules or 3½ molecules of acetylacetone were present according to whether the weaker or the stronger solution were used. The weaker solution was used for salts of bivalent metals, the stronger for the tervalent metals.

Ordinary reagents were then added to see whether or not the presence of acetylacetone inhibited their action.

Silver Nitrate.—Slight cloudiness on adding the acetylacetone; sodium chloride precipitates silver chloride.

Mercurous Nitrate.—Acetylacetone reduces to metal.

Mercuric Chloride.—No visible change on adding acetylacetone; hydrogen sulphide precipitates mercuric sulphide.

Lead Nitrate.—No apparent change; hydrogen sulphide, sodium chloride, potassium chromate, sodium carbonate, and potassium sulphate give the usual precipitates.

Copper Sulphate.—Colour changes from blue to green; hydrogen sulphate, potassium thiocyanate, and sodium hydroxide gave the usual reactions.

Cadmium Sulphate.—No visible change; hydrogen sulphide precipitates cadmium sulphide.

Potash Alum.—No apparent change; sodium hydroxide, sodium hydrogen phosphate, and ammonium hydrogen phosphate give the usual precipitates.

Chromium Sulphate.—No visible change. With ammonia and sodium hydrogen phosphate precipitates are formed on keeping. Ammonium hydrogen phosphate gives no precipitate: the precipitate with sodium hydroxide is soluble in excess of the reagent.

Ferric Alum.—Colour changes to deep red (deeper than thiocyanate) on adding acetylacetone. Ammonia produces a precipitate on keeping for some time. Sodium hydrogen phosphate gives no precipitate in the cold, but the solution is considerably lightened in colour, and a precipitate is produced on boiling. Precipitates are obtained with sodium hydroxide and ammonium hydrogen phosphate.

Zinc Sulphate and Manganese Sulphate.—No visible change; usual reactions with sodium hydrogen phosphate, sodium carbonate, hydrogen sulphide, and sodium hydroxide.

Nickel Sulphate.—No visible change; usual reactions with sodium hydroxide and hydrogen sulphide (after adding ammonia).

Cobalt Sulphate.—No visible change; hydrogen sulphide precipitates cobalt sulphide after adding ammonia. Sodium hydroxide gives a blue precipitate, which turns brown on keeping.

35. "*Viscosity and Association.* Part IV. *The Viscosity of the Aromatic Amines.*" By FERDINAND BERNARD THOLE.

This work was undertaken with the primary object of finding whether substitution in the benzene ring affects the viscosity of the aromatic amines in the same way as in the case of the phenols.

At the same time the range of amines previously studied by Mussell, Thole, and Dunstan has been increased considerably.

A large number of amines, substituted both in the amino-group and in the benzene nucleus by different groups, have been examined in the pure state at 55° and in amyl acetate solution.

The results show a number of interesting parallels with the corresponding phenolic derivatives, especially as regards the influence of the carbethoxyl and nitro-groups, but frequently the analogies are hidden by the influence of other factors, the important effects of which are shown much more clearly in this series than in the other types of compounds hitherto examined.

36. "*Influence of the Constitution of Tertiary Bases on the Rate of Formation of Quaternary Ammonium Salts.*" Part I. By EBENEZER REES THOMAS.

The author has measured the reaction velocities of certain aromatic tertiary bases with allyl bromide, and, in some cases, benzoyl bromide, at 40° in N/10-absolute alcoholic solution.

Twenty-one bases have been examined, and certain general conclusions as to the influence of the nature and position of substituents were indicated.

37. "*Some Blue Iron Cyanogen Compounds.*" By HERBERT ERNEST WILLIAMS.

The precipitation of a blue ferric ferrocyanide from a ferrocyanide of an alkali metal always contains some alkali metal in combination which cannot be removed by washing. Several blue compounds were prepared under different conditions from the alkali metal ferrocyanides, and analysed after being thoroughly washed and dried.

In all cases the alkali metal was found to be present in definite ratio to the ferrocyanogen, and blue iron cyanogen compounds of complex formulæ were obtained.

Manganomanganic ferrocyanide is produced by the action of concentrated nitric acid on the white manganous ferrocyanide; it forms a dark brown granular powder.

38. "*Some Properties of Carbon Monoxide.*" By RICHARD WILLIAM MERRIMAN.

Three hundred litres of carbon monoxide were prepared by slowly delivering pure formic acid below the surface of concentrated sulphuric acid kept at 60°. The gas was passed through four Drechsel flasks containing 30 per cent sodium hydroxide, and was collected over water in a large gas-holder. Although always described as an odourless and tasteless gas, this specimen had a perfectly definite metallic odour and taste. The idea occurred to the author that it might contain a small quantity of the unknown formic anhydride. This substance would have the properties of an aldehyde, so the following experiment was performed. The gas was bubbled through a series of Drechsel flasks containing the following solutions:—Sodium hydroxide, decolorised rosaniline, sodium hydroxide (2), Fehling's solution, and ammoniacal silver nitrate. The decolorised rosaniline was not altered, but the silver nitrate and Fehling's solution were at once reduced.

Carbon monoxide prepared in the following ways also possessed similar properties.

(a) *From Oxalic Acid.*—Two hundred and thirty cc. of pure sulphuric acid were added to 100 grms. of crystallised oxalic acid. The temperature rose to 45°. Effervescence commenced at 65° and slow evolution at 90°. A regular stream of gas was evolved by keeping the temperature at 110°. The gas was washed with four portions of 30 per cent sodium hydroxide and passed through four soda-lime towers. It was passed through three Drechsel flasks containing Fehling's solution and three containing ammoniacal silver nitrate. All showed reduction.

(b) *From Potassium Cyanide.*—Pure sulphuric acid was dropped on to 200 grms. of potassium cyanide in lumps. The cyanide turned brown and rapidly evolved gas. The gas was passed through four Drechsel flasks containing 30 per cent sodium hydroxide, four soda-lime towers, and two Drechsel flasks containing 20 per cent silver nitrate. The first two portions of sodium hydroxide turned reddish brown and finally black. The last silver nitrate showed no precipitate of silver cyanide. The gas possessed the

same odour, taste, and reducing properties as the other specimens.

(c) *From Pure Sulphuric Acid and Sodium Formate.*—External heat was unnecessary except at the end of the preparation. The gas was washed as before and had the same properties.

(d) *From 70 per Cent Sulphuric Acid and Sodium Formate.*—The formate dissolved at 70°; slow evolution of gas commenced at 85°, but did not become rapid below 115°; the final temperature was 135°. The gas, treated as before, possessed the same properties.

(*e*) Smaller quantities of gas were prepared from lactic acid and malic acid with similar results.

(*f*) *From Carbon Dioxide and Carbon.*—As a final test, 40 litres of carbon monoxide were prepared by slowly passing pure carbon dioxide through a tube 80 cm. long packed with charcoal heated to bright redness. In this experiment formic anhydride could not have been produced. The carbon dioxide from a Kipp's apparatus was passed through two wash-bottles containing sodium carbonate solution and two containing pure sulphuric acid. The resulting gas was washed as before and possessed the same properties.

It follows that pure carbon monoxide possesses a perfectly characteristic odour and taste, and readily reduces Fehling's solution and ammoniacal silver nitrate solution. It has no action on decolorised rosaniline.

PHYSICAL SOCIETY.

Annual General Meeting, February 14th, 1913.

Prof. A. Schuster, F.R.S., President, in the Chair.

The Report of the Council was taken as read.

The Report of the Treasurer was read and adopted.

Votes of thanks to the auditors, proposed by Dr. W. H. Eccles and seconded by Dr. H. Borns; to the Officers and Council for the way in which they served the Society, proposed by Prof. G. H. Bryan and seconded by Mr. R. J. Sowter; and to the Governors of the Imperial College of Science for the use of their premises, proposed by Mr. W. Noble and seconded by Prof. C. H. Lees, were carried unanimously.

The Officers elected for the ensuing year were as follows:—

President—Prof. A. Schuster, Ph.D., F.R.S.

Vice-Presidents—Those who have filled the office of President, together with F. E. Smith; Prof. C. H. Lees, D.Sc., F.R.S.; Prof. T. Mather, F.R.S.; A. Russell, M.A., D.Sc.

Secretaries—W. R. Cooper, M.A.; S. W. J. Smith, M.A., D.Sc.

Foreign Secretary—Prof. S. P. Thompson, D.Sc., F.R.S.

Treasurer—W. Duddell, F.R.S.

Librarian—S. W. J. Smith, M.A., D.Sc.

Other Members of Council—Prof. C. G. Barkla, D.Sc., F.R.S.; Prof. P. V. Bevan, M.A.; W. H. Eccles, D.Sc.; Prof. J. W. Nicholson, M.A., D.Sc.; Major W. A. J. O'Meara, C.M.G.; T. C. Porter, M.A., D.Sc.; Prof. the Hon. R. J. Strutt, F.R.S.; W. E. Sumpner, D.Sc.; R. S. Whipple; R. S. Willows, M.A., D.Sc.

Prof. Schuster, in thanking the meeting for his re-election, mentioned that some of the seven Fellows the Society had lost by death during the past year had been known to him personally, and referred in particular to Osborne Reynolds, Major General Festing, and the Earl of Crawford.

Continuing, he stated that he would like to take the opportunity of paying a tribute to the memory of Captain Scott, and to speak of the scientific work which he had organised for his expedition. There never was any expedition which was so well thought out in advance, or so well fitted out for scientific purposes. Captain Scott spent a good deal of time and trouble in carrying out his intentions, and whether he got to the Pole or not, or whether his expedition was a success or not, he was determined that it should be a scientific success. It was the organisation of the scientific side of the expedition which enabled Amundsen to get ahead of Scott, and which delayed Scott's enterprise. As far as that side of the expedition was concerned, it had been most successful, and he knew that there would be complete records of magnetic observations and photographic illustrations of the expedition almost without a break. He could not speak of the biological and geological work which had been accomplished, but Captain Scott had been so careful in selecting his observers that he felt confident that in those directions, also, valuable records would have been obtained.

Prof. G. H. Bryan, Sc.D., F.R.S., then read a paper on "*The Dynamics of Pianoforte Touch.*"

The author discussed Helmholtz's and Kaufmann's theories of the vibrations of a pianoforte wire excited by impact, with special reference to the effects obtainable with the modern pneumatical piano-players and player-pianos, and the common widespread belief that these can never reproduce the touch of the human fingers. While the rendering of many commercial piano-players in the hands of an average performer bears little resemblance to the performance of a professional pianist, the author finds that there is generally believed to be a certain element missing even in music played by a skilled performer on a first-class modern piano-player, this missing element being commonly associated with what is described as "touch." In view of the great value of piano-players to lovers of music, it thus becomes interesting to examine more closely what is meant by "touch," and whether it is capable of being reproduced to a greater extent than hitherto upon pneumatically controlled pianos.

The question turns very largely on the extent, if any, to which the *quality* of individual notes can be varied by striking the notes in different ways. Such a possibility involves the inferences that (*a*) the intensities of the fundamental tone and its several harmonics are capable of independent variation; (*b*) these variations can only be produced by varying the behaviour of the pianoforte hammer while it is in contact with the string, for example, by lengthening or shortening the duration of contact; (*c*) such an effect can only be produced by rapid time variations of the pressure applied to the keys while they are being depressed—*e.g.*, by a fairly rapid decrease or increase of pressure produced by smartly striking or heavily pressing on the key.

The author finds that Kaufmann's investigation fails to account for any such effects, and that difficulties arise, even when the equations are modified so as to take account of impressed forces on the hammer comparable with those due to gravity. On the other hand, he describes experiments which appear to indicate beyond all reasonable doubt the existence of such effects of "touch," and which certainly demonstrate the possibility of reproducing them by means of the modern "pneumatic" instrument. For this purpose the author's piano-player, which is a first-class instrument of the "Standard" type, but *with the whole keyboard under one common control*, was fitted with an "auxiliary lever" for which a patent application has been filed. This lever operates directly on the face of the auxiliary regulating bellows, and the air-tension in the bellows can be regulated by means of a sliding weight placed on the lever, or by applying hand pressure to the lever itself. In this way *the touch of the human hand can be transmitted directly to the keys of the piano.* So far as the experiments go, they indicate that even if the lever is worked in conjunction with suitable expression marks, as could be done by a person of moderate experience, increased breadth of contrast is obtained. While by varying the position of the load independently of the pedalling a variety of dynamical effects can be produced, which can further be increased by hand control.

A short sharp pressure produces a bright ringing treble

with a light bass, a sustained pressure produces a rich bass with a soft treble; the general character of the tone being suitably described as "metallic" in the first case and "woody" in the second. A very conspicuous feature of these experiments is the marked differentiation which they show between notes in different parts of the scale, especially in chords, the notes of which are accurately ranged (as is unfortunately often not the case in music rolls). The duration of the pressure required to produce the maximum effect on a particular note of the piano varies continuously from the treble to the bass end, being least in the treble and greatest in the bass, and by means of this natural or dynamical differentiation notes in a particular part of a chord at any part of the scale can be accented independently of the rest.

Whether it is possible to vary the quality of individual notes is a point that can only be tested by playing single notes as opposed to chords. The differences that can be effected can only be noticed by a trained ear; in the author's experiments it has been found that some persons notice *very marked* differences, others notice very slight differences, others no differences at all. The differences are probably as conspicuous as those between a stopped string and a harmonic on the violin. It is not always easy to produce these differences for purposes of demonstration, though it is often easier to do so in the course of playing through a suitable composition. In any case the author finds that the effects can be obtained more easily with a pneumatic player fitted with auxiliary lever than in striking the keys with fingers. When the lever is disconnected the change observed affords some indication of the origin of the popular belief in the limitations of the pneumatically played piano.

Unlike the gramophone, aeroplane, motor-car, and cinematograph, the modern piano-player has been conspicuous by the absence of reference to it in scientific and technical journals. The present paper, which arises out of an attempt to obtain a closer degree of approximation to *playing the piano* with these instruments indicates that they open up some interesting problems in the study of acoustics.

Mr. A. CAMPBELL, speaking as a musician, said that Prof. Bryan's invention largely increased the capabilities of the mechanical piano-player, as it gave the person who guided the machine the power of accenting particular notes at any part of the keyboard. If the *loudness be kept constant*, the differences in quality of tone that can be obtained from a piano are quite infinitesimal compared with the difference given by two pipes of different stops on an organ, and are of negligible value in musical art, although their importance is so commonly magnified by fancy and by professional humbug. Piano music has to depend for its variety on factors other than difference in tone quality. The comparative constancy in tone quality could, no doubt, be demonstrated objectively by means of phonautograph records.

Mr. W. H. ECCLES entirely disagreed with Mr. Campbell, and considered the difference was most marked, and considered that Prof. Bryan's lever made a great difference in the contrast obtainable, but he thought it would be an improvement to be able to make the soft passages softer.

The PRESIDENT remarked that the explanation of the difference of tone of a note according as to the manner in which it was struck—such as, for instance, between the touch of a learner and a skilled player—must interest many even of those who were not musical.

Mr. G. H. BERRY (communicated remarks), as a practical pianoforte maker, considered it was impossible to vary the time of contact of the hammer with the string, since when the hammer is in contact with the string the key is entirely disconnected from it. Only the striking velocity could be varied. He certainly thought Prof. Bryan's invention gave greater control over this striking velocity. Kaufmann's investigation neglects a point of primary importance to the pianoforte, and that is that the sound heard is emitted by the forced vibration of the sound-board and not by the string. The former has a natural frequency of its own, and is set in vibration by the blow of the hammer transmitted through the strings. This natural frequency is rapidly damped, some experiments of his own showing that only about six waves were emitted, but the first two or three had a larger amplitude than the forced vibrations caused by the string.

Mr. V. LOUGH (communicated remarks) certainly thought Prof. Bryan's invention enabled a skilled operator to make a great improvement in the rendering of the music, but there seemed to be none of the clear singing tones and delicate touch effects which can be produced by a good pianist. Apparently these are still beyond the range of the mechanical player.

Prof. G. H. BRYAN, in reply, stated that it was difficult to gauge the loudness of the soft passages on a strange piano in a strange room. As regards the effects of the harmonics the interesting thing was to see whether the entire difference in quality of a tone of a note played with the human hand and by a mechanical player could be accounted for in terms of the harmonics.

NOTICES OF BOOKS.

Oxidations and Reductions in the Animal Body. By H. D. DAKIN, D.Sc., F.I.C. London, New York, Bombay, and Calcutta: Longmans, Green, and Co. 1912.

IN this monograph the subject of oxidations and reductions in the animal body is considered from the point of view of the structure of the substance undergoing change, and the results which have been obtained during the last few years are summarised. The general methods employed in characterising the intermediate and end products in such reactions occurring in the animal body are first described in outline, and then the different groups of substances, fatty acids, unsaturated acids, &c., are taken up in turn, and the definite results which have been obtained are stated, while many provisional conclusions which cannot be regarded as either proved or disproved by the evidence as yet accumulated are also pointed out. The α-amido and amino acids are fully treated, this being the region in which much of the author's work has lain, but other compounds are not by any means neglected, and the monograph is a useful addition to the Biochemical Series.

Questions on Newth's Inorganic Chemistry. By GEORGE D. TIMMONS, B S., Ph.C. London, New York, Bombay, and Calcutta: Longmans, Green, and Co. 1912.

THIS collection of questions on Newth's "Inorganic Chemistry" covers the book chapter by chapter, and aims at enabling the student to discover whether he has thoroughly mastered the facts enumerated in it. Very little scope is given for his originality or reflective power, and if he had read the book carefully he should have no difficulty in answering these perfectly simple and straightforward questions, which might be of great assistance to candidates for examination in testing their knowledge and giving them practice in writing answers.

A Dictionary of Applied Chemistry. By Sir EDWARD THORPE, C.B., LL.D., F.R.S. Volume III. Revised and Enlarged Edition. London, New York, Bombay, and Calcutta: Longmans, Green, and Co. 1912.

THE third volume of the revised and enlarged edition of this "Dictionary of Applied Chemistry" covers the letters G R to O I L S, and contains many important articles of considerable length. Such are those on Metallography, Milk, Oils and Fats, &c. In every respect the dictionary is complete and up-to-date, and it is unsurpassed as a work of reference on Applied Chemistry.

Modern Inorganic Chemistry. By J. W. Mellor, D.Sc. London, New York, Bombay, and Calcutta: Longmans, Green, and Co. 1912.

In this book the author endeavours to present the subject in such a way as to train the student's observations and logical faculties to their fullest extent, while at the same time leading him to cultivate his imagination and his critical powers. The point of view of the book is essentially modern, and the teacher will find it of great use to him as a work of reference, while the historical and philosophical treatment of the subject will inevitably make it appeal greatly to the thoughtful student. Physico-chemical considerations are given much prominence, but the use of higher mathematics is avoided as far as possible. The diagrams, especially those representing electrical apparatus and methods, are very clear and instructive, and the author's style of writing possesses a certain vividness which should help to impress the facts and principles mentioned on the student's mind. Questions from the papers set by various public examining bodies are included.

Industrial and Manufacturing Chemistry: Organic. Edited by Geoffrey Martin, Ph.D. (Rostock), M.Sc.(Bristol), B.Sc. (London), F.C.S. London: Crosby Lockwood and Son. 1913.

This text-book on industrial and manufacturing chemistry covers the whole subject, and is intended equally for the use of the student, lecturer, manufacturer, consulting chemist, and chemical engineer. In endeavouring to meet all the needs of these very different classes of readers the editor has perhaps rather over-reached himself, although he and his collaborators, who are all experts in the several branches of the subject on which they write, have done their best not to subordinate the claims of one class to those of another. As a general work of reference, giving an outline which may serve as a basis for more detailed study, the book is not by any means without its advantages, one of the chief of which is the fact that the minor industries are not neglected. The editor claims that he has been able to give his readers much information which has not been published before, and has pointed ut some problems the investigation of which may lead to important industrial developments. The analysis of many of the products described is included, but the details are not always very full, and the analytical chemist would probably have to fall back upon some other work. References to literature and statistics are plentiful and complete, and the specialist will find it a great convenience to be able to refer to the bibliographies for the titles of books or articles which would be likely to contain any detailed information that he might require.

A Systematic Course of Practical Science for Secondary and other Schools. Book I. *Introductory Physical Measurements*. By Arthur W. Mason, B.Sc., B.A. (Lond.). London: Rivingtons. 1912.

An introductory course of physical measurements, suitable for boys beginning science work, is described in this book. Very minute directions as to methods of writing descriptions of experiments and recording results are given, and a high ideal of accuracy is put before the student. Some teachers may possibly prefer to modify the directions to a certain extent, but they will hardly be able to improve upon the general plan. The course begins with measurements of length, giving various exercises in finding diameters, circumferences, &c., and in drawing graphs. The principles of the wedge, lever, and beam balance are then investigated, and the measurement of areas and volumes and the determination of density are discussed. The section on experiments with liquids describes some very instructive experiments, and the pressure of the air is clearly and, considering the scope of the book, fully treated. The experiments on the flow of liquids, too, are well chosen and should prove stimulating and interesting.

A Handbook of Sugar Analysis. By C. A. Browne, Ph.D. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1912.

A wide selection of methods of sugar analysis is to be found in this book, those which have been perfected in recent times being given special prominence, although the older processes are not passed over. The author, from his extensive experience of analysis in the New York Sugar Trade Laboratory, is in a position to give valuable information about the applicability and limitations of each method, which will greatly add to the value of the book from the point of view of the more or less inexperienced chemist. Methods of calculating results are explained by means of many fully worked out numerical examples, and the book is well supplied with tables. In Part II. some account is given of the occurrence, methods of preparation, properties, and reactions of the different sugars, and references are made to the synthesis of sugars.

Scientific Method. By F. W. Westaway. London, Glasgow, and Bombay: Blackie and Son, Ltd. 1912.

This is a thoroughly interesting book, which, though written In the first place for science teachers, will undoubtedly appeal to a much wider circle of readers. It is divided into four main sections. In the first, the philosophy of scientific method is discussed, and after an introductory chapter on the terminology and elementary principles of philosophy, some account is given of the parts played by Aristotle, Bacon, Plato, and other philosophers in developing it. Book II. deals with the logic of scientific method, and in this part the chapters on measurement and error will make a special appeal to the science teacher. In Book III. some of the most typical investigations of famous men of science are reproduced in the actual words of the original publications, and finally the applications of scientific method in the class room are discussed. Many practically useful hints are given on the arranging of a syllabus for scientific work and the most satisfactory way of developing the student's powers as much as possible in all directions, and even experienced teachers will find the section full of valuable matter.

Industrial Chemistry. Edited by Allen Rogers and Alfred B. Aubert. London: Constable and Co., Ltd. 1912.

This book contains a number of articles, covering practically all the chemical industries, written by experts, and showing the present state of each industry in America and describing the most modern American methods and processes. Commercial statistics and data are freely given, and the book is of an essentially practical type. It covers a wide range of subjects, and the space allotted to each is necessarily very restricted; thus only eighteen pages are given to dye-stuffs and their application. Hence the authors of the several sections have been unable to go at all deeply into their subjects, and the specialist who referred to the book would undoubtedly feel the need of fuller details. It is a pity, too, that quite unnecessary and uninstructive illustrations, such as the view of full gasometers, are allowed to take up room which might be used to better advantage.

Experimental Mensuration. By H. Stanley Redgrove, B.Sc. (Lond.), F.C.S. London: William Heinemann. 1912.

A thoroughly sound course of practical mathematics is given in this book, which exhibits a most advanced and modern method of attacking the subject. Intended for students in technical schools, it might well be used much more widely if certain parts of it were slightly curtailed. It contains the substance of Euclid, the student being instructed in methods of arriving at certain truths experimentally, and then the deductive proof of the same fact is

either given in full or indicated for the student to work out for himself. The old formal method of writing out propositions is entirely given up, and the order of presentation of the subjects is no longer that dictated by formal logic, but by common sense. The boy who learns from the book will get a knowledge of plane and solid geometry, trigonometry, the mensuration of pyramids, prisms, &c.; he will learn the use of mathematical instruments and some physical apparatus, and his knowledge will be thoroughly practical. When once it has been recognised that with a very large number of students the attempt to teach logic and geometry simultaneously by a formal deductive course is doomed to failure, the great value of books of this kind will be more fully recognised than it is at present.

The Elements of Qualitative Chemical Analysis. By JULIUS STIEGLITZ. In Two Volumes. New York: The Century Co. 1912.

IN Volume I. of this work the fundamental principles of qualitative analysis and their application are treated very thoroughly. Osmosis, the theory of ionisation, the law of mass action, chemical and physical equilibrium are discussed in short chapters, in which details of some lecture experiments are also included. The text is distinctly difficult in places, but the book is not intended for young beginners, and advanced students should be able to acquire from it a thorough knowledge of the principles of qualitative analysis, viewed from the most modern point of view. References to original papers are given in abundance, those which are to be regarded as suitable for the reading of second-year college students being specially distinguished. Volume II. is the Laboratory Manual intended to accompany the first volume. In it the practice of qualitative analysis is studied. The book is interleaved with blank paper, on which the student is recommended to answer the questions which are interspersed in the text and to record his observations. The common organic acids are included among the acid radicles, and if there is possibly a rather bewildering amount of detail, on the other hand no well known test or method of separation is omitted, and the treatment of the subject represents the very acme of thoroughness and completeness.

Die Fabrikation des Russes und der Schwarze. ("The Manufacture of Soot and of other Blacks"). By Dr. HIPPOLYT KÖHLER. Third Edition. Braunschweig: Friedrich Vieweg und Sohn. 1912. (7 M.).

THE manufacture of various forms of amorphous carbon is fully treated in this work, the second edition of which was exhausted very soon after publication. The author has to record a rapid advance during recent years in methods of manufacturing lamp and other blacks, and has made every effort to give detailed descriptions of modern practice. He discusses the testing and examination of soot and the blacks, and gives some account of the various applications of amorphous carbon in making pigments, &c.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clv., No. 25, December 16, 1912.

This number contains no chemical matter.

Atti della Reale Accademia dei Lincei. Vol. xxi. (ii.), No. 9, 1912.

Spontaneous Formation of Iodo-base containing Iodine in a Pentatomic Cyclic Nucleus.—L. Mascarelli.—When OO'—di-iodosodiphenyl or its tetrachlorine derivative is left in presence of water for some months a substance capable of giving a yellow precipitate with sulphur dioxide is obtained. This precipitate is the iodide of diphenylene iodonium, $\begin{matrix} C_6H_4 \\ | \\ C_6H_4 \end{matrix}\!\!>\!I.I$. Thus an atomic transposition of the iodine occurs by which a cyclic substance containing iodine in a closed chain is obtained. Apparently the chloride first reacts with water to give an iodoso derivative, which then undergoes simultaneous oxidation and reduction.

Unstable Nitrites Fixed by Means of Organic Bases.—G. Scagliarini.—The author has continued his study of the formation of stable compounds of nitrites and organic bases, and has found that mercury, cadmium, and zinc nitrites all give compounds with hexamethylene tetramine. The formulæ are—

$$2Hg(NO_2)_2.8H_2O.3C_6N_4H_{12}$$
$$Cd(NO_2)_2.2H_2O.C_6N_4H_{12}$$
$$Zn(NO_2)_2.2H_2O.C_6N_4H_{12}.$$

MEETINGS FOR THE WEEK.

MONDAY, 3rd.—Royal Institution, 5. General Meeting.
—— Royal Society of Arts, 8. (Cantor Lecture). "Coal Gas as a Fuel for Domestic Purposes," by Francis W. Goodenough.
—— Society of Chemical Industry, 8. "Notes on Chinese Antimony Ores, Crude and Regulus," by W. R. Schoeller. "Notes on Thermometry," by J. H. Coste.

TUESDAY, 4th.—Royal Institution, 3. "The Movements of the Stars," by Prof H. H. Turner, D.Sc., F.R.S.

WEDNESDAY, 5th.—Society of Public Analysts, 8. "Accurate Determination of Carbon Dioxide in Carbonates," by F. S Sinnatt. "Egyptian Butter and Semna," by S. H Trimen. "Bacterial Testing of Disinfectants—a Practical Criticism," by C. T. Kingzett and R. C. Woodcock. "Quick and Improved Method for the Estimation of Boric Acid in Milk and Cream," by F W. Richardson and W. K. Walton. "The Moisture in some English, Colonial, and Foreign Butters during 1910-1912, with a Note on the Mitchell-Walker Moisture Test," by L. Gowing-Scopes.
—— Royal Society of Arts, 8. "The Development of Research Work in Forest Products," by E. Russell Burdon.

THURSDAY, 6th.—Royal Institution, 3. "Surface Energy," by W. B. Hardy, F.R.S., &c.
—— Royal Society of Arts, 4.30. "The City of Karachi," by J. Forrest Brunton.
—— Royal Society. "Automatic Method for the Investigation of the Velocity of Transmission of Excitation in Mimosa," by J. C. Bose. "Evolution of the Cretaceous Asteriodea," by W. K. Spencer. "Preliminary Note on the Fossil Plants of the Mount Potts Beds, New Zealand, collected by Mr. D. G. Lillie, Biologist to Capt Scott's Antarctic Expedition in the *Terra Nova* in 1911," by E. A. Newell Arber. "Trypanosomes found in the Blood of Wild Animals living in the Sleeping Sickness Area, Nyassaland," "Trypanosome Diseases of Domestic Animals in Nyassaland,—II., *Trypanosoma Caprae* (Kleine)," and "Morphology of various Strains of the Trypanosome causing Disease in Man in Nyassaland—I, the Human Strain," by Surg.-Gen. Sir David Bruce, Majors D. Harvey and A. E. Hamerton, and Lady Bruce.
—— Chemical, 8.30. "Quinonoid Salts of Nitranilines," by A. G Green and F. M. Rowe. "Nomenclature of Sugar Derivatives," by J. C. Irvine. "Partially Methylated Glucoses—Part I., 6-Monomethyl Glucose and 3:5:6-Trimethyl Glucose; Part II., 2:3-Dimethyl-α-glucose and 2:3-Dimethyl-β-glucose," by J. C. Irvine and J. P. Scott. "Pipitzahoic Acid," by F. G. P. Remfry. "Polybromides in Nitrobenzene Solutions," by A. F. Joseph. "Cyaphenine," by J. E. Mackenzie.

FRIDAY, 7th.—Royal Institution, 9. "Photography of the Paths of Particles ejected from Atoms," by C. T. R. Wilson, F.R.S., &c.

SATURDAY, 8th.—Royal Institution, 3. "The Properties and Constitution of the Atom." by Prof. Sir J. J. Thomson, O.M., F.R.S., &c.

THE CHEMICAL NEWS.

VOL. CVII., No. 2780.

A NEW METHOD FOR THE ESTIMATION OF HYPOCHLORITES.

By HERBERT G. WILLIAMS.

RONCALI and Roberts (*Chem. Central.*, 1904, i., 1294) suggest the estimation of hypochlorites by adding (slowly) a known volume of the hypochlorite solution to a boiling solution of hydrazine sulphate in dilute sulphuric acid, and measuring the volume of nitrogen liberated, the "available chlorine" being double this.

Apparently chlorine is first set free by the acid, and acts upon the hydrazine thus :—

$$N_2H_4 + 2Cl_2 \rightarrow N_2 + 4(HCl).$$

The following method is certainly simpler, and appears quite accurate enough for most purposes. The hypochlorite solution is titrated with a solution of hydrazine sulphate containing 3·2535 grms. per litre (each cc. = 0·0008 grms. of oxygen = 0·003546 grms. of chlorine), the end-point being determined by iodide-starch paper as in the well-known arsenite method of Penot. If the alkali always present with hypochlorites is not sufficient to neutralise the sulphuric acid liberated, sufficient is added to ensure this; otherwise the results are irregular. Sodium bicarbonate is the most suitable for the purpose, as it has little, if any, action on the liberated iodine (see Stollé, *Journ. Prakt. Chem.*, 1902, lxvi., 332). The action appears to be :—

$$N_2H_4 + 2(MOCl) \rightarrow N_2 + 2(H_2O) + 2(MCl).$$

In order to test the accuracy of this method two portions (25 cc.) of the hypochlorite solution were taken; one titrated with N/10 As_4O_6, the other with the $N_2H_4.H_2SO_4$, the two burettes having been previously calibrated against one another. Some results are shown below :—

1. *Sodium Hypochlorite.*

As_4O_6 used (cc.).	N_2H_4 used (cc.).
19·29	19·34
19·28	19·30
19·24	19·25
19·13	19·12
19·12	19·13
19·10	19·11

Greatest difference .. 0·05 cc. = 0·25 per cent
Average difference .. 0·015 cc. = 0·075 per cent

2. *Bleaching Powder.*

As_4O_6 used (cc.).	N_2H_4 used.
18·63	18·60
18·60	18·57
18·60	18·59
18·60	18·57
18·52	18·54
18·50	18·56

Greatest difference .. 0·06 cc. = 0·33 per cent
Average difference .. 0·02 cc. = 0·11 per cent

The variations in the numbers read vertically arise from he fact that frequently a considerable time elapsed between two titrations with the same reagent; but in all cases titration with the one followed immediately after the other.

It will be noted that the agreement is not quite so good in the last two sets of readings, probably owing to the fact that the (unfiltered) bleaching powder solution is not homogeneous.

The solution of hydrazine sulphate is much easier to prepare than N/10 As_4O_6, and it appears to keep better.

Browne and Shetterly (*Journ. American Chem. Soc.*, 1908, p. 53) find that when hydrazine sulphate is oxidised by chlorates or by free chlorine, ammonia and hydrazoi acid are formed; but no trace of these could be detected in the mixtures after titration.

Attempts have been made to verify the equation by measuring the evolved nitrogen, but the possible errors make it much less satisfactory than the titration method.

Robert Gordon's College, Aberdeen.

THE DETERMINATION OF TIN IN BRONZES.

By F. IBBOTSON and L. AITCHISON.

THERE are many disadvantages in the usual way of estimating tin in its alloys with copper. This method utilises the precipitation of the tin as metastannic acid by opening out of the alloy with concentrated nitric acid. The precipitate is always impure, containing considerable amounts of copper and lead, which must be estimated in some way; either directly and so obtain the tin by difference, or else by the direct estimation of the tin from the impurities. The former direct estimation of the impurities usually involves the fusion of the stannic oxide obtained by the ignition of the metastannic acid, with either a mixture of sulphur and sodium carbonate or with sodium thiosulphate alone. In either case the operation is not a nice one, and usually requires at least one repetition. The second method is generally that of fusion with potassium cyanide to obtain a bead of tin, which is not always easy to obtain, and which when obtained is not pure.

A much more satisfactory method is to estimate the tin directly in the precipitated metastannic acid without any previous ignition or weighing. The precipitate is completely soluble in sulphuric acid containing about half its volume of water. It is not entirely soluble in hydrochloric acid—the larger pieces of precipitate being taken up quite easily, but the finely divided portion not being taken into complete solution.

For a bronze containing about 10 per cent of tin, take 1 grm. of coarse drillings and attack with 10 to 15 cc. of nitric acid, sp. gr. 1·4. The quantity of alloy should be chosen so as to give approximately 0·1 grm. of tin. Allow the action to proceed to completion, and then evaporate the free acid by taking to a paste, after which add 75 cc. of hot water and boil for a few minutes. Allow the precipitate to settle, and then filter hot through a tightly-packed filter of asbestos pulp, keeping as much of the precipitate as possible in the flask, and washing by decantation with hot water containing a small quantity of nitric acid. There is no necessity to wash with any thoroughness, as the copper filtrate must be discarded. It cannot be employed for the estimation of the copper, as it does not contain it all, and the subsequent operations with the precipitate do not allow of the recovery of the contained copper. Wash finally with water until free nitric acid is removed, and then transfer the whole of the filter and precipitate to the flask containing the greater portion of the residue, using as little water as possible in the transference (less than 20 cc. if possible). Next add a volume of concentrated sulphuric acid equal to that of the water employed, and boil the solution, taking due precautions against bumping. After boiling for three minutes add 50 cc. of concentrated hydrochloric acid, and again boil for two minutes. The solution should now be free from any turbidity. Add about 1 grm. of very finely powdered antimony, boil for about a minute, and then cool rapidly under the tap, allowing a current of carbon dioxide to pass through the solution during the whole operation. When quite cold, add starch, and titrate at once with N/20 iodine solution, finishing the titration as quickly as possible.

The important part of the later proceedings is the management of the proportions of the two strong acids. The following series of titrations, performed under exactly similar conditions on equal volumes of a standard solution of stannic ammonium chloride to which varying quantities

of acid had been added, show the limits of safety in the proportions :—

Tin solution.	Hydrochloric acid (conc).	Sulphuric acid (conc.).	N/20 iodine.
Cc.	Cc.	Cc.	Cc.
25	25	5	22·0
25	25	10	21·9
25	25	15	21·9
25	25	25	21·9
25	50	25	21·9
25	20	—	22·0

If the proportion of sulphuric acid to hydrochloric acid is still further increased there is serious interference. When the proportions are five hydrochloric to three sulphuric there is no appreciable effect, and so the amounts employed above are quite safe.

A dilution of the solution has no ill effect upon the titration, rather the reverse, but if the bulk is increased in any serious degree there is considerable difficulty in ensuring a perfect distribution of the antimony through the whole of the solution during the boiling. The presence of the asbestos in no way interferes, the end-point of the titration being perfectly sharp and plain.

A method of an entirely different kind for the separation of copper and tin is based upon the different behaviour of these elements towards hydrazine salts in caustic alkaline solutions. Jannasch and Biedermann (*Ber.*, 1900, p. 631) have shown that copper can be quantitatively precipitated in the metallic form from such solutions by means of hydrazine sulphate or hydrochloride, whilst tin in the stannic condition remains in solution under the same conditions. The authors have been able to get most gratifying results by modifying the procedure advocated by Jannasch and Biedermann, which was found unsatisfactory when applied to the analysis of bronzes for tin (and copper).

0·5 grm. of the drillings are dissolved in 10 to 15 cc. of aqua regia, and the solution diluted with an equal volume of water. A solution of sodium hydrate is added until most of the free acid is neutralised without the formation of a precipitate, and the mixture is then heated to boiling. In a large Erlenmeyer flask 20 grms. of sodium hydrate are dissolved in about 300 cc. of water, and this solution is also heated to boiling, whereupon 2 to 3 grms. of hydrazine hydrochloride (not sulphate) are added to it. The mixture of copper and stannic chlorides is then transferred to a separating funnel, and is delivered in drops into the strongly alkaline solution whilst the latter is vigorously shaken. The copper is precipitated as metal, with previous but momentary formation of cuprous oxide. The mixture is now digested for about fifteen minutes until the vigorous evolution of gas subsides, and the copper then filtered out. After washing with hot water the filtrate is concentrated, after acidifying with hydrochloric acid, and the tin determined by the method already described, or gravimetrically by precipitation as stannic sulphide and ignition to oxide. The copper can also be easily determined in any one of the numerous ways to which the metal as such so readily lends itself. The results are accurate.

The authors hope to make a further communication on this separation, which they employ for the determination of copper in white metal alloys.

Metallurgical Department,
University of Sheffield.

Contardi's Glycerotriphosphoric Acid.—P. Carré. —Contardi has stated that when a molecule of glycerin is etherified by 3 molecules of phosphoric acid, glycerotriphosphoric acid, $C_3H_5(PO_4H_2)_3$, is formed quantitatively. On repeating the experiments, however, the author finds that the reaction really gives glycerodiphosphoric acid, $C_3H_5OH(PO_4H_2)_2$, glycerophosphoric acid, and a diether of the formula PO_4R_2H. About 50 per cent of the phosphoric acid remains in the free state.—*Comptes Rendus*, clv., No. 26.

THE RARE EARTHS OF THE CAROLINA MONAZITE SANDS.

By C. JAMES.

According to some writers the yttrium earths, derived from the monazite sands of Carolina, contain an element which prevents the rapid fractionation of this mixture. It occurred to the writer that it would be extremely interesting to apply the bromate method to these earths. It is true that the yttrium metals from monazite have been submitted to this method, but in previous work they were added to euxenite earths and the whole treated together. The conditions were therefore different, and no conclusions could be drawn.

The material used in this work was obtained by treating a solution of monazite earths with potassium sulphate. The latter salt was added in an insufficient quantity to precipitate all the cerium metals. It was hoped that by leaving a fair amount of neodymium, &c., in solution, that nearly all the samarium and gadolinium contained in the original mineral would be left unprecipitated. The filtrate was treated with oxalic acid, and the resulting oxalate was the starting point for this study.

These earths were prepared in this manner by Dr. H. S. Miner, to whom the author desires to express his sincere thanks.

The oxalates were converted into oxides by ignition, after which they were dissolved in nitric acid. Since cerium was present in considerable amount, some of the original oxalate was boiled with the solution to reduce all cerium in the ceric condition. The nitrate solution was then poured into large earthenware vessels, and the whole allowed to settle. The clear liquid was syphoned off and mixed with magnesium nitrate. (The magnesium nitrate was prepared from ignited magnesite by dissolving it in nitric acid. The neutral solution was then treated with a slight excess of magnesite at the boiling-point. This threw down the small quantities of iron and aluminium that were present. These hydroxides were separated from the solution by filtration through cloth).

The double magnesium nitrates were fractionally crystallised from water acidified with nitric acid. Lanthanum, cerium, and praseodymium rapidiy passed into the less soluble fractions. The intermediate crystals carried nearly all the neodymium together with very small quantities of praseodymium. The mother-liquors, which crystallised badly, owing to the accumulation of iron and aluminium in addition to the yttrium earths, showed fairly weak absorption bands of neodymium, stronger bands of samarium, and bands of medium strength of dysprosium, holmium, and erbium. The thulium red band was not distinct.

These mother-liquors were diluted, and all the earths precipitated as oxalates by adding a boiling solution of oxalic acid. The precipitate was filtered off, washed, and ignited to oxide.

According to previous work carried out by the writer, the above oxides should be very rich in samarium and gadolinium. As the spectroscope revealed the presence of considerable samarium, it was deemed advisable to separate most of these elements before the study of the yttrium earths should be carried on. In order to accomplish this the oxides were dissolved in nitric acid, and the simple nitrates obtained in this way were submitted to fractional crystallisation from nitric acid of 1·3 specific gravity. The spectroscope indicated that neodymium was inclined to spread itself over a wide range of fractions. Large amounts of material formed the less soluble portions, and these appeared to consist almost entirely of samarium, gadolinium, and neodymium. The absorption spectrum showed the presence of the first and last, and judging by the intensities there must have been a lot of earth in the mixture, giving no absorption bands. The spectra of dysprosium, holmium, erbium, and thulium were absent. Probably nearly all the europium and a good deal of the

terbium, which the original earths contained, passed into this portion of nitrates.

The mother-liquors from the less soluble nitrate crystals showed a spectrum containing strong bands of dysprosium, holmium, and erbium. Thulium was extremely weak. Small quantities of neodymium and samarium, and probably a minute amount of gadolinium (europium and terbium), remained with the yttrium earths.

The nitrate solution containing the yttrium metals was diluted and precipitated by means of oxalic acid. The whole was allowed to stand for some time, so as to make sure that the precipitation was complete. The oxalates were filtered off, washed, dried, and converted into anhydrous sulphates by mixing with a slight excess of sulphuric acid and heating, with considerable stirring, until fumes of the acid ceased to be evolved.

The ignited sulphate was dissolved by stirring with cold water in a copper vessel which was surrounded by cold water. Copper was used since it is a good conductor of heat and prevented a rapid increase in temperature, due to the hydration of the sulphates. The stirring was best carried out by a propeller of copper fitted about an inch from the bottom. This propeller was connected by a copper shaft to a small wooden pulley wheel, which could be worked by a hot-air motor. When working upon a smaller scale, a large round bottom flask immersed in cold water and stirred by means of an air blast was found to be very efficient.

The sulphate solution was gradually added to barium bromate covered with water, and contained in very large porcelain dishes (James, *Journ. Am. Chem. Soc.*, xxx., 182). The mass was well stirred, and, when the supernatant liquid proved to be free from sulphates, it was filtered. The barium sulphate remaining upon the filter was thoroughly washed. The original filtrate and washwater were evaporated to crystallisation and the whole fractionally crystallised from water solution.

(Note.—When very rare substances are converted into bromates, by treating barium bromate with a sulphate, it is important to remember that the resulting barium sulphate entrains a varying amount of the sulphate of the rare earth. Hence it is often necessary to regain this material by one of the well-known methods).

When four fractions had formed, the first and last were examined by their absorption spectra. The least soluble, fraction I., contained neodymium and samarium, and owing to its pale colour probably gadolinium was present in quantity. The bands of erbium, holmium, and dysprosium were practically absent. Fraction 4, the most soluble, showed an entirely different spectrum; only the merest trace of neodymium was visible; the bands of erbium, holmium, and dysprosium were strong; thulium could also be detected by its absorption spectrum.

After continuing the fractionation for a longer period, it was observed that the small amounts of ytterbium (ytterbium, lutecium, and celtium) and thulium had passed into the most soluble fraction. This was then removed from the series. By studying the remaining fractions by means of the spectroscope, it could be seen that erbium together with yttrium was rapidly separating from holmium, dysprosium, and yttrium. Yttrium coming between the erbium and holmium earths naturally accompanies both. In the fractions following dysprosium, neodymium was found. As the least soluble end was reached, the bands of samarium became stronger.

It can be seen from the above that these Carolina earths can be separated just as easily as those from another mineral, such as gadolinite. The fractions between dysprosium and samarium appeared to be especially interesting, since neodymium seems to insert itself between some members of the yttrium earths. This should be somewhere near the point where terbium would accumulate. Since the separation of gadolinium, terbium, dysprosium, and holmium is somewhat difficult, the fractionation of this portion of the series was kept going for a few weeks more. Two series of operations could be carried out during the day. As soon as the least soluble fractions showed only traces of neodymium they were placed aside. The mother-liquors were removed when the absorption bands became weak, since this indicated a concentration of yttrium. The removal of the latter element could be followed by observing the intensity of the dysprosium and holmium absorption, which increased with the concentration of these elements. Finally, when dysprosium began to pass into the mother-liquor in considerable quantity, each fraction was carefully examined.

The fraction having the greatest solubility gave very strong bands of holmium and dysprosium. Erbium and neodymium were absent. The next casserole contained a similar mixture together with a trace of neodymium. The crystals following showed a marked increase of the neodymium content, while the absorption spectrum of holmium was much fainter than that of dysprosium. In the next fraction neodymium was very intense, dysprosium strong, and holmium just visible. Further along the series neodymium remained intense, but dysprosium was not seen. As the least soluble end was approached, the spectrum of samarium made its appearance, and as this became stronger neodymium rapidly faded away.

It was decided first to examine thoroughly the neodymium that came nearest to the fraction showing only a faint holmium spectrum. The crystals were dissolved, and the resulting solution diluted and stirred with solid sodium sulphate. The double sulphates were filtered off, the filtrate poured into boiling sodium hydroxide, and the whole filtered. The hydroxides remaining upon the funnel were washed, dissolved in nitric acid, and precipitated by oxalic acid. The oxalates upon ignition gave a deep brown coloured oxide, which, when in solution in nitric acid, showed a fairly strong dysprosium spectrum; that of neodymium was weak, and the holmium absorption in the green was just perceptible. Therefore, judging from the colour of the oxide and the absorption spectrum, the yttrium earths consisted of gadolinium with much dysprosium, a little terbium, and traces of holmium. The writer is of the opinion that the bromate method would be of great service for the concentration of terbium. And in order to settle the question an investigation is being commenced, using many kilogrms. of terbium material.

The results of this study indicate that Carolina monazite contains, in addition to lanthanum, cerium, praseodymium, and neodymium, considerable samarium, gadolinium, and yttrium; small amounts of dysprosium, holmium, and erbium; and minute amounts of europium, terbium, thulium, and ytterbium, &c. It is also interesting to note that erbium occurs in much smaller quantities than holmium and dysprosium. This fact probably accounts for the apparent anomaly, found by some workers upon certain fractions, as shown by the equivalent determination, when compared with some other mineral such as gadolinite or euxenite.

The writer would recommend the oxalates from the more soluble double sulphates as a source for samarium, gadolinium, europium, terbium, dysprosium, and holmium.

Note 1.—A similar article will shortly appear upon the rare earths contained in samarskite from Sankara Mica Mine of Mysore, India. The author desires to express his thanks to the Syndicate for their generosity in supplying him with a very large amount of this mineral.

Note 2.—It becomes necessary to correct another point with regard to the bromate method of fractionation. In order to observe how the separation of holmium and dysprosium is proceeding, one must convert into the nitrates before observing the absorption spectrum, and the solution should be concentrated. This work upon the Carolina monazite has shown that the bromate method is after all a very good one for the separation of these elements. It possesses the advantage that no hydrolysis takes place, as is the case with the ethyl-sulphates, even when one uses great care.

Durham, N.H.

A VOLUMETRIC METHOD FOR THE DETERMINATION OF THORIUM IN THE PRESENCE OF OTHER RARE EARTHS. THE ANALYSIS OF MONAZITE SAND.

By F. J. METZGER and F. W. ZONS.

WHEN an excess of ammonium molybdate solution is added to a solution of a thorium salt under proper conditions of temperature and acidity, thorium is quantitatively precipitated as molybdate. Other rare earths, such as cerium, lanthanum, neodymium, praseodymium, erbium, yttrium, gadolinium, &c., give no precipitation whatever under similar conditions.

The above facts, observed by one of us some years ago, form the basis of the method described in this paper.

The thorium molybdate precipitate is somewhat gelatinous in character, pale yellow in colour, and settles very slowly. In our earlier experiments an attempt was made to filter off the precipitated thorium and make the determination gravimetrically, but owing to the slimy nature of the precipitate, filtration and washing were impossible.

The usual indicators for molybdenum were tried with the hope that a direct titration of the thorium could be made, but without success.

Cazeneuve (*Comptes Rendus*, 1900, cxxxi., 346) found diphenyl carbazide to be a sensitive reagent for certain metallic salts, as those of copper, mercury, iron, and also for chromates. Lecoq (*Jour. Chem. Soc.*, 1904, lxxxvi., 369) used an alcoholic solution of diphenyl carbazide as a test for molybdenum. A pink coloration is produced, and the author states that the test is more sensitive after the solution of diphenyl carbazide has been allowed to stand for some time. In order to test the applicability of this indicator, a number of titrations of pure thorium nitrate solution were made, and the results obtained were concordant. The indicator is used "outside" on a white indented tile, the end of the titration being marked by the appearance of a pink coloration which lasts about fifteen seconds. Some experience is required to identify the end-point. This is gained in standardising the ammonium molybdate against a standard thorium nitrate solution. *It is necessary to use a solution of the indicator at least two weeks old*, as the freshly prepared solution requires a considerable excess of molybdenum to produce a pink coloration. The titration is made at room temperature, in the presence of acetic acid.

The solutions used in the experimental part of the work were as follows:—

Thorium Nitrate.—A solution of pure thorium nitrate accurately standardised by precipitating as oxalate, igniting, and weighing as oxide.

Potassium Permanganate.—An approximately 0·1 N solution standardised against specially prepared Mohr's salt; 1 cc. = 0·005835 Fe.

Ammonium Molybdate.—Approximately 20 grms. ammonium molybdate per litre. In order that the thorium-molybdenum ratio in the precipitate might be determined, this solution was carefully standardised by acidifying, reducing in a Jones reductor, and titrating with permanganate as usual. The average of a number of titrations gave 10 cc. molybdate solution = 28·2 cc. $KMnO_4$. Assuming the reduction to be $MoO_3 \Rightarrow Mo_{24}O_{37}$, then 1 cc. molybdate solution = 0·0098136 Mo.

Indicator.—0·5 grm. of diphenyl carbazide dissolved in 200 cc. of 95 per cent alcohol and allowed to stand at least two weeks before using. The solution when ready for use should be yellowish in colour, but show no pink tinge.

(A convenient and satisfactory method for the preparation of diphenyl carbazide is as follows:—Add 23 grms. of phenyl-hydrazine to 7 grms. of urea in a flask, and heat in an oil-bath at 160–170° for six hours, using a reflux air condenser. Allow to cool, add 50 cc. ethyl ether, heat on a hot plate for one hour, decant and add 50 cc. ethyl ether, heating for two hours longer; a white precipitate is obtained, the residue of reagents going into solution in the ether. Decant the ether, dissolve the precipitate of impure diphenyl carbazide in alcohol and reprecipitate by pouring into excess of water; decant the water, redissolve the precipitate in alcohol, and pour again into excess of water. Filter on a Büchner funnel, wash and dry at 105°. Yield, 14·3 grms. diphenyl carbazide. M. p. 150°–151°. *The diphenyl carbazide is white when first precipitated but in time turns brownish yellow. A trace of impurity causes it to turn pink; hence all vessels, dropping tubes, &c., must be scrupulously clean. The indicator, when on the white tile, should be yellowish or brownish yellow.*)

In order to obtain uniformity in acidity of the solutions for titration and to have the conditions analogous to those obtaining in the analysis of a monazite sand, a number of determinations were made as follows:—

A known amount of thorium solution, or thorium solution with the addition of other rare earths, was placed in a casserole and evaporated to dryness on a water-bath. To the dry residue 4 cc. of glacial acetic acid were added, then 300 cc. of water. When the salts were dissolved, the cold solution was titrated with ammonium molybdate. The molybdate solution should be added a few tenths of a cc. at a time, with vigorous stirring after each addition, finally finishing drop by drop. The end-point is reached when a drop of the solution produces the previously described pink coloration when brought in contact with a few drops of indicator on a white tile. After a little experience the end-point can be determined with great accuracy. Table I. shows the results obtained.

TABLE I.

No.	ThO_2. Grm.	Other earths present.	Molybdate solution. Cc.
1.	0·0500	—	3·65
2.	0·0500	—	3·65
3.	0·0852	—	6·4
4.	0·0852	—	6·4
5.	0·0852	—	6·5
6.	0·1000	—	7·35
7.	0·1000	—	7·4
8.	0·0500	0·1 Nd_2O_3	3·9
9.	0·0500	0·1 Pr_2O_3	3·9
10.	0·0500	0·1 La_2O_3	3·9
11.	0·0852	0·1 La_2O_3	7·1
12.	0·0852	0·1 La_2O_3	7·1
13.	0·0852	0·1 Pr_2O_3	7·2
14.	0·0852	0·1 CeO_2	7·1
15.	0·0852	0·1 grm. each of Ce, La, Pr, Nd.	7·1
16.	0·0852	0·1 grm. each of Ce, La, Pr, Nd.	7·2
17.	0·0852	0·1 grm. each of Y, Gd, Er.	7·2
18.	0·0852	0·1 CeO_2	7·1
19.	0·0852	0·1 „	7·1
20.	0·0852	0·1 „	7·1
21.	0·0852	0·1 „	7·1
22.	0·0852	0·2 „	7·1
23.	0·0852	0·3 „	7·2
24.	0·0852	0·3 „	7·1
25.	0·0852	0·3 „	7·1
26.	0·0852	0·6 „	7·1
27.	0·0852	0·6 „	7·1
28.	0·0852	0·6 „	7·2
29.	0·0852	0·6 „	7·2
30.	0·0852	4·26 „	7·1
31.	0·0852	4·26 „	7·1

In titrations Nos. 11 to 21, the total dilution varied between 150 cc. and 300 cc., and 1 grm. of sodium acetate was added to each to counteract any possible mineral acid present. These results show that although the consumption of molybdate solution was greater when other

rare earths were present, the volume of molybdate was the same whether the added rare earth was small or large in amount. From this it was assumed that the concentration of acetic acid was insufficient to entirely prevent the precipitation of rare earths other than thorium.

Another set of titrations with increased acidity resulted as follows :—

No.	Dilution.	Sodium acetate.	Acetic acid (glacial).	ThO_2.	Molybdate.
	Cc.	Grm.	Cc.	Grm.	Cc.
32.	300	1	10	0·0852	6·4
33.	300	1	10	0·0852	6·5
34.	300	1	20	0·0852	6·4
35.	300	1	20	0·0852	6·4
36.	300	1	20	0·0852 (*a*)	6·45
37.	300	1	20	0·0852 (*a*)	6·4

(*a*) Contained 0·1 grm. each of Pr, La, Nd, Gd.

The values here obtained are in satisfactory agreement with those obtained with thorium alone, the increased acidity preventing interference by the other rare earths.

Composition of Precipitate.—Taking the value of the $KMnO_4$ already given (1 cc. = 0·005835 Fe) and its equivalent in terms of molybdate solution (28·2 cc. $KMnO_4$ = 10 cc. molybdate) then 1 cc. molybdate = 0·0098136 Mo. The average of the eleven titrations of thorium alone (Nos. 1 to 7 and 32 to 35) gives 0·0815 ThO_2 = 6·095 cc. molybdate, or a ratio Th : Mo = 1 : 2·017. Similarly, the average of titrations 36 and 37 with impurity present gives Th : Mo = 1 : 2·03. It is therefore probable that the precipitate is a normal thorium molybdate.

Analysis of Monazite Sand.—In order to test the accuracy of the method for the determination of thorium in monazite sand, samples of North Carolina and Brazil sands which had been analysed by the fumaric acid method, the thiosulphate-ammonium oxalate method, and the metanitrobenzoic acid method were analysed. (For a description of these methods the reader is referred to the original articles, F. J. Metzger, *Journ. Am. Chem. Soc.*, xxiv., 901 ; A. C. Neish, *Ibid.*, xxvi., 780).

The volumetric method is carried out as follows:—To 1 grm. of the powdered sand in a porcelain crucible is added 10—15 cc. of concentrated sulphuric acid. After several hours heating the crucible is cooled and the contents transferred, a little at a time and with constant stirring, to about 700 cc. water which has been cooled to near 0°. After standing several hours (over night if convenient) to insure complete solution of the sulphates, the solution is filtered and the residue washed thoroughly with cold water. The filtrate is nearly neutralised with dilute ammonia, 50 cc. of a cold saturated solution of oxalic acid added, and allowed to stand over night. The oxalates are filtered and washed with a dilute oxalic acid solution. When thoroughly washed, transfer precipitate and paper to a beaker, add 20—25 cc. of strong potassium hydroxide solution, and heat to boiling. Dilute, filter, and wash with hot water. Dissolve the precipitate of rare earth hydroxides off the filter by means of hot dilute nitric acid. Evaporate to dryness on a water-bath. Add a few cubic centimetres of water, and again evaporate to dryness to remove free acid. To the dry residue add 20 cc. glacial acetic acid, dilute with 300 cc. water, add 1 grm. sodium acetate, and stir until dissolved. Titrate at room temperature with standard ammonium molybdate solution as already described. The results obtained are given in Table II.

The following were analysed by the volumetric method but not checked by other methods :—

No. 626 North Carolina	4·84	4·84
No. 631 North Carolina	5·11	5·11

Conclusions.

1. At room temperature thorium is precipitated quantitatively from a cold acetic acid solution (20 cc. glacial acetic acid and 300 cc. water) by means of ammonium molybdate.

2. Other rare earths found in monazite sand are not precipitated under the conditions defined in "1."

3. The ratio of thorium to molybdenum (1 : 2·017 and 1 : 203) indicates that the precipitate is a normal thorium molybdate.

4. By observing proper conditions of acidity, thorium may be accurately titrated by means of ammonium molybdate. Other rare earths have no effect on this titration.—*Journal of Industrial and Engineering Chemistry*, iv., No. 7.

Table II.

	Percentage ThO_2.			
	Volumetric method.	Meta-nitrobenzoic acid method (*a*).	Fumaric acid method.	Thiosulphate ammonium oxalate method.
	No. 3 Brazil.			
	4·80	4·76	4·85	4·90
	4·80	4·85	—	—
	4·98	4·99	—	—
	4·99	—	—	—
	4·99	—	—	—
	4·99	—	—	—
	5·05	—	—	—
	5·05	—	—	—
	5·05	—	—	—
Average .	4·97	4·87	4·85	4·90
	No. 363 Brazil Concentrate.			
	5·58	5·60	5·70	5·63
	5·65	5·65	—	—
	5·65	5·67	—	—
	5·65	5·70	—	—
	5·65	5·73	—	—
	5·72	—	—	—
	5·72	—	—	—
Average .	5·66	5·67	5·70	5·63
	No. 625 Brazil.			
	4·85	—	4·88	—
	4·92	—	4·89	—
	4·92	—	—	—
	4·98	—	—	—
	5·1	—	—	—
	5·3 (*b*)	—	—	—
Average .	4·95			

(*a*) Analyses by this method were made by Dr. A. C. Neish.

(*b*) The authors are unable to account for this high result; it is omitted in the average.

Supposed Isomerism of Potassium Ferricyanide.—O. Hauser and E. Biesalski.—Locke and Edwards have described a green modification of potassium ferricyanide which they call the β-form. They state :—(1) The α-form exists as red crystals, while the β-form exists as small greenish crystals; (2) the solution of the α-form is reddish yellow, that of the β form olive-green ; (3) the heavy metal salts of the β-form differ in colour from those of the α-form. The authors' experiments confirm these conclusions in the main, but their solutions of the β-form and the heavy metal precipitates obtained from it were never of a pure colour, and they believe that the green form is red prussiate of potash mixed with small quantities of prussian blue, and its solution is a colloidal solution of prussian blue in a solution of that salt.—*Berichte*, xlv., No. 16.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, February 20th, 1913.

Sir ARCHIBALD GEIKIE, K.C.B., President, in the Chair.

PAPERS were read as follows:—

"*Studies on Enzymes Action.* XIX. *Urease: a Selective Enzyme.* II. *Observations on Accelerative and Inhibitive Agents.*" By Prof. H. E. ARMSTRONG, F.R.S., M. S. BENJAMIN, and E. HORTON.

"*Nervous Rhythm arising from Rivalry between Antagonistic Reflexes: Reflex Stepping as Outcome of Double Reciprocal Innervation.*" By Prof. C. S. SHERRINGTON, F.R.S.

"*Liberation of Ions and the Oxygen Tension of Tissues during Activity.*" (Preliminary Communication). By H. E. ROAF, M.D., D.Sc.

The combination Ag | AgCl | Muscle | Ringer Solution | HgCl | Hg shows an increased negative charge on the silver when the muscle contracts. The explanation is that there is either an increase in concentration of chlorine ions or the liberation of a positive ion with high migration velocity. In the former case the chlorine ions cause an increased negative charge at the silver chloride, silver contact. In the latter case the rapid diffusion of the positive ion from the muscle into the Ringer Solution leaves the silver with a negative charge.

The combination Pt | MnO_2 | Muscle | Ringer Solution | HgCl | Hg shows an increased positive charge on the platinum when the muscle contracts. This result must be due to an increase in hydrogen ions.

The combination Pt | Muscle | Ringer Solution | HgCl | Hg can be used as an indicator of the oxygen tension in contracting muscle. The platinum must be protected from the oxygen in the air.

"*Contributions to the Biochemistry of Growth. The Glycogen Content of the Liver of Rats bearing Malignant New Growths.*" By W. CRAMER and J. LOCHHEAD.

Glycogen disappears more rapidly from the liver of tumour-bearing rats than from the liver of a normal rat. Since observations on the gaseous metabolism showed that there is no increased oxidation of carbohydrate material in tumour-bearing animals, the results confirm the conclusion arrived at previously from observations on pregnant animals, that in growth carbohydrate material is used for the synthesis of protoplasm.

"*On Changes in the Glomeruli and Tubules of the Kidney accompanying Activity.*" By Prof. T. G. BRODIE, F.R.S., and J. J. MACKENZIE, M.B.

CHEMICAL SOCIETY.

Ordinary Meeting February 20th, 1913.

Prof. PERCY F. FRANKLAND, LL.D., F.R.S., President, in the Chair.

THE PRESIDENT referred to the loss sustained by the Society through death of:—

Otis Coe Johnson (elected March 4th, 1897, died June 6th, 1912); Theodore David Lichtenstein (elected February 21st, 1879, died October 23rd, 1912); George Matthey (elected May 3rd, 1870, died February 14th, 1912); B. Venkata Rao (elected December 7th, 1911, died 1912).

Certificates were read for the first time in favour of Messrs. Horace George Battye, 28, Roman Place, Roundhay, Leeds; Noël Guilbert Stevenson Coppin, M.Sc., Rydal Mount, Runcorn, Cheshire; Harold Davies, 18, Windsor Road, Ilford; Fritz Haber, Post Lichterfelde, 3, Berlin-Dahlem; Darab Dinsha Kanza, M.A., India Institute of Science, Bangalore; Emmanuel F. Kur, Learansa, Devonshire Road, St. Anne's-on-Sea; Bhaichand Anupchand Mehta, M.A., Indian Institute of Science, Bangalore; Francis Martin Potter, B.Sc., 6, Stavordale Road, Highbury, N.; Arthur Samuel Robinson, B.Sc., King's School, Pontefract; Reginald William Rusby, Westgate, Greenhill Road, Moseley, Birmingham; Hormusji Kharshedji Sahiar, M.A., Indian Institute of Science, Bangalore; William James Stansfield, 12, Bell Hatt Terrace, Saville Park, Halifax.

A certificate has been authorised by the Council under By-law I. (3) in favour of Ferrand Paget, Bombay Burma Trading Corporation, Ltd., Bangkok, Siam.

The following announcements were made:—

1. That the following changes in the Officers and Council were proposed by the Council:—

President to retire—Prof. Percy F. Frankland.

Secretary to retire—Prof. A. W. Crossley.

Foreign Secretary to retire—Dr. Horace T. Brown.

Vice-Presidents to retire - Dr. M. O. Forster and Prof. A. Liversidge.

Ordinary Members of Council to retire—Prof. W. A. Bone, Mr. A. R. Ling, Dr. A. McKenzie, and Dr. J. C. Philip.

As President—Prof. W. H. Perkin.

As Vice-Presidents who have filled the office of President—Prof. H. E. Armstrong, Prof. A. Crum Brown, Sir William Crookes, Sir James Dewar, Prof. H. B. Dixon, Prof. Percy F. Frankland, Dr. A. G. Vernon Harcourt, Prof. R. Meldola, Dr. H. Müller, Prof. W. Odling, Sir William Ramsay, Prof. J. Emerson Reynolds, The Right Hon. Sir Henry E. Roscoe, Sir Edward Thorpe, and Sir William A. Tilden.

As Treasurer—Dr. Alexander Scott.

As Hon. Secretaries—Dr. Samuel Smiles and Dr. J. C. Philip.

As Foreign Secretary—Prof. Arthur W. Crossley.

As Vice-Presidents—Prof. H. B. Baker, Dr. G. T. Beilby, Dr. Horace T. Brown, Prof. E. J. Mills, Prof. G. T. Morgan, and Prof. W. Jackson Pope.

As New Ordinary Members of Council—Dr. G. Barger, Mr. E. J. Bevan, Prof. F. G. Donnan, and Prof. K. J. P. Orton.

2. That Fellows were invited to attend a meeting of the Faraday Society to be held in the rooms of the Chemical Society on Wednesday, March 12th, from 4 to 6 and 8 to 10 p.m., when a discussion on "Colloids and their Viscosity" would take place.

Prof. J. Millar Thomson, Dr. Samuel Rideal, and Prof. J. J. Dobbie were elected Auditors to audit the Society's Accounts.

A ballot for the election of Fellows was held, and the following were subsequently declared elected:—Theodore William Gull Acland; Neil Kensington Adam, B.A.; William Beath; Crellyn Colgrave Bissett, B.Sc.; Albert Brier, M.Sc.: Percy Charles Burr, B.Sc.; John Hugh Christie, B.Sc.; Harold Reginald Septimus Clotworthy, B.A., B.Sc.; John Albert Cockshutt, M.Sc.; Charles George Cutbush; Daniel James Davies, B.Sc.; Roland Doumin; James Henry Edmondson; Thomas Lenton Elliott; Ulick Richardson Evans, B.A.; Albert Edward Garrett, B.Sc.; Tin Kari Ghose, B.A., L.M.S.; Robert Gilmour, B.Sc., Ph.D.; George Watson Gray; Douglas Henville; James Arthur Hewitt, B.Sc.; William Joseph Holt; Alfred Leslie Howells, B.Sc.; Thomas James Kirkland, B.Sc.; Peter Thomas Leitch; Daniel William Lloyd, B.Sc.; Walter Cyril Loynes; Alexander Killen Macbeth, M.A., B.Sc.; Henry Stephen Martin; Aylmer Henry Maude; Joseph Horsnell May; Ernest Joseph Mumford; Paul Murphy; Jonathan Harold Naylor, M.Sc.; Thomas Joseph Nolan, M.Sc.; Jonathan Parker; Cornelius Theodore Pollard, B.Sc.; William Norman Rae, B.A.; Hermann Horace Roskin, B.Sc.; William Slessor Simpson,

M.A., B.Sc.; John Walter Smith, B.Sc.; Harold Victor Taylor; Percy James Thompson; Bertrand Turner, B.Sc.; Thomas Willoughby Turnill; Edward Webb, B.Sc.; Siddons Siddons Wilson; Hubert Rogers Wood.

Of the following papers, those marked * were read :—

*39. "*The Mode of Combustion of Carbon.*" By Thomas Fred Eric Rhead and Richard Vernon Wheeler.

The authors, in continuation of their work on the combustion of carbon, whereby they showed that carbon dioxide and carbon monoxide are produced together when carbon is burned, described experiments made to account for this simultaneous production of the two oxides.

It was shown that carbon, at all temperatures up to 900° and probably above that temperature, has the power of pertinaciously retaining oxygen. This oxygen cannot be removed by exhaustion alone, but only by increasing the temperature of the carbon during exhaustion. When quickly released in this manner, it appears, not as oxygen, but as carbon dioxide and carbon monoxide. The proportions in which it appears in these two oxides when completely removed depends on the temperature at which the carbon has been heated during oxygen-fixation.

It was shown also that no physical explanation alone can account for this "fixation" of oxygen, but that, in all probability, it is the outcome of a physico-chemical attraction between oxygen and carbon. Physical, inasmuch as it seems hardly possible to assign any definite molecular formula to the complex formed, which indeed exhibits progressive variation in composition; chemical, in that no isolation of the complex can be effected by physical means.

Decomposition of the complex by heat produces carbon dioxide and carbon monoxide. At a given temperature of decomposition these oxides make their appearance in a given ratio. Further, when a rapid stream of air at a given temperature is passed over carbon (which has previously been saturated with oxygen at that temperature), carbon dioxide and carbon monoxide appear in the products of combustion in nearly the same ratio as they do in the products of decomposition of the complex at that temperature.

It is therefore suggested that the first product of combustion of carbon is a loosely-formed physico-chemical complex, which can be regarded as an unstable compound of carbon and oxygen of an at present unknown formula, C_xO_y. It is probable that no definite formula can be assigned to this complex.

Discussion.

Prof. Smithells, after commending the previous paper by the same authors for its new observations and as a lucid and trustworthy account of the history of the controverted question of the combustion of solid carbon, said that he saw no *prima facie* objection to the doctrine of C_xO_y.

The case of the combustion of solid carbon was essentially different from that of carbon in gaseous compounds. In that case observations on the rate of explosion of cyanogen mixed with different proportions of oxygen, and analysis of the gases in the flame of cyanogen, as well as spectroscopic evidence, pointed to carbon monoxide as the first product. The argument relating to the more likely co-operation of two molecules rather than three, $C_2N_2+O_2$ rather than $C_2N_2+2O_2$, as the first transaction in a molecular system, was not applicable to the case of solid carbon. The molecule of solid carbon, judging from the very high volatilisation temperature of the element, was probably of great atomic complexity, and it could easily be believed that such an atomic complex in the stationary position of the solid state, rained upon by a shower of oxygen molecules, could, at a moderate temperature, result in the production of C_xO_y, where x and y might be very high numbers. The complex, of course, at a higher temperature would be resolved into the proportions of CO and CO_2 conformable to the equilibrium at that temperature of the system : solid carbon, carbon monoxide, carbon dioxide.

Prof. Donnan asked what period of time the authors waited after pumping off the gases in order to determine the final pressure of carbon monoxide and carbon dioxide in equilibrium with the assumed complex C_xO_y. As the carbon monoxide and dioxide were produced initially *in* the adsorbed layer or in the solid carbon, the establishment of equilibrium might take some time.

Prof. Bone, replying on behalf of the authors, said that the point raised by Prof. Donnan was dealt with in the paper; the authors' evidence for the formation of the complex C_xO_y was largely cumulative, and could only be judged by a detailed study of the experimental work as a whole. Speaking personally, he had still an open mind on the subject, although, like Prof. Smithells, he had no *à priori* difficulty in accepting the idea of the primary formation of the said complex. With regard to the President's remarks about the probable cause of the spontaneous combustion of coal, he thought that it might be attributed to the oxidation of the constituents extractable by pyridine, which decomposed on heating below 700°, yielding chiefly paraffin hydrocarbons and little hydrogen (see Burgess and Wheeler's papers on "The Volatile Constituents of Coal"), and which were probably derived from the resinous matter in the vegetable *débris* from which the coal originated.

*40. "*The Interaction of Bromine and the Sulphides of β-Naphthol.*" (Part II.). By Thomas Joseph Nolan and Samuel Smiles.

The diacetyl derivative of the unstable sulphide was converted into the anhydride by treatment with boiling acetic anhydride and sodium acetate. This anhydride—termed *iso*naphthathioxin—was found to be different from that obtained by dehydrating the stable sulphide. With bromine it yielded a dibromonaphthathioxin, which was identical with the product formed by the interaction of this halogen and the acetyl derivative of the unstable sulphide. Previous experiments (*Trans.*, 1912, ci., 1420) had shown that with bromine this sulphide yields the dibromosulphonium-quinone, and it was concluded that the different result now obtained with the acetyl derivative is due to liberation of acetyl bromide at a preliminary stage of the interaction, the two cases being represented as follows :—

$$C_{20}H_{12}S(OH)_2 + Br_2 = O:C_{10}H_6:S:C_{10}H_6:O + 2HBr.$$
$$C_{20}H_{12}S(OAc)_2 + Br_2 = O:C_{10}H_6:S:C_{10}H_6:O + 2AcBr.$$

Independent experiment proved that in the presence of acetyl bromide and bromine the sulphonium-quinone yields the dibromonaphthathioxin.

The diacetyl derivative of the stable sulphide did not react with bromine under the conditions chosen in these experiments.

It was also pointed out that the properties of the hydroxyl groups in the unstable sulphide correspond with those of an unsaturated tertiary alcohol.

41. "*The Nomenclature of the Rhamnose Group and of other Substances Related to the Aldohexoses.*" By Hugh Marshall.

In view of the definite establishment, by E. Fischer and K. Zach (*Ber.*, 1912, xlv., 3761), of the configuration of "rhamnose" and "*iso*rhamnose," the author suggested the adoption of a systematic nomenclature for the group, based on that of the aldohexose group, so as to avoid the multiplication of novel names and the use of prefixes "*iso*," &c. It was proposed that the name *rhamnose* should be used for the whole isomeric group, and be prefixed by the stem of the name of the aldose having the same configuration; the individual names would then be: —(*d*- and *l*-) *mannorhamnose* (ordinary rhamnose), *glucorhamnose* (*iso*rhamnose or *iso*rhodeose), *idorhamnose*, *gulorhamnose*, *galactorhamnose*, *talorhamnose*, *allorhamnose*, *altrorhamnose*. It was also suggested that a similar principle should be applied in the case of other hexose derivatives which would have eight pairs of stereoisomerides; at least, to those containing any two different

terminal groups out of the following four:—CO_2H, CHO, $CH_2{\cdot}OH$, CH_3, such as the isomerides of glucuronic acid.

42. "*Some Green Iron Cyanogen Compounds.*" By HERBERT ERNEST WILLIAMS.

A solution of ammonium ferrocyanide when boiled in contact with the air, forms a dull green deposit, which has the formula $Fe_2'''Fe''(NH_4)_8[Fe''(CN)_6]_4,3H_2O$; a similar potassium compound, $Fe_2'''Fe''K_8[Fe''(CN)_6]_4,6H_2O$, is produced by adding very dilute hydrochloric acid gradually to a boiling solution of potassium ferrocyanide, and by substituting ammonium chloride solution for the hydrochloric acid the compound $Fe_2'''Fe''(NH_4)_7K[Fe(CN)_6]_4,3H_2O$ is produced. Somewhat similar compounds of ferrosoferric ferrocyanides of a dull blue colour were prepared, agreeing with the formulæ $Fe'''Fe_2''Na_6[Fe(CN)_6]_4,6H_2O$ and $Fe_2'''Fe_2''(NH_4)_6[Fe(CN)_6]_4,8H_2O$.

These compounds can be considered as molecular compounds of the ferric double salts and ferrous ferrocyanides, as in the case of the blue iron cyanogen compounds.

Ferric ferrocyanide when boiled with concentrated nitric acid is converted into the green compound, $Fe_7'''[Fe''Fe'''(CN)_{12}]_3,54H_2O$.

By boiling ferric potassium ferrocyanide with nitric acid a green compound, $Fe_{13}'''[Fe''Fe_3'''(CN)_{24}]_3\ 100H_2O$, is obtained; this compound is also produced by passing chlorine through freshly precipitated ferric ferrocyanide.

The addition of ferric salts to a solution containing one equivalent of ferrocyanide and more than three equivalents of ferricyanide yields a fine dark green precipitate of the composition $Fe_{29}'''K_3[Fe''Fe_2'''(CN)_{18}]_9,210H_2O$.

When ferrous potassium ferrocyanide, obtained by distilling potassium ferrocyanide with dilute acid, is oxidised whilst still boiling with excess of nitric acid, the violet compound, $Fe_3'''K_2[Fe_2'\ Fe'''(CN)_{18}],6H_2O$, is produced.

Cupric ferrocyanide when boiled with concentrated nitric acid also yields a ferroferricyanide of the composition $Cu_7[Fe''Fe'''(CN)_{12}]_2,30H_2O$.

From a consideration of the formation of these green compounds, and particularly of the copper compound, it is probable that they are ferric ferroferricyanides, and not ferrosoferric ferricyanides.

43. "*Catalytic Decomposition of Hydrogen Peroxide.*" By GWEN DYER and ALICE BARBARA DALE.

It has been generally accepted on the authority of Bredig and Müller von Berneck (*Zeit. Phys. Chem.*, 1900, xxxi., 289) that the catalytic decomposition of hydrogen peroxide in aqueous solution proceeds as a unimolecular reaction:—

$$H_2O_2 \rightarrow H_2O + O.$$

Bredig's observations seem to have been made with solutions of about 0·0007 grm. of hydrogen peroxide per cc. The present authors find that in a solution containing 0·0025 grm. of hydrogen peroxide per cc. the action appears to be a bimolecular one:—

$$2H_2O_2 \rightarrow 2H_2O + O_2.$$

Fifty cc. of the solution were kept at constant temperature of 20°, 2 cc. of Bredig's colloidal platinum solution being added as a catalyst. Successive quantities of 5 cc. were titrated with potassium permanganate at exactly noted intervals, varying from five to ten minutes.

Taking $C_1, C_2, C_3 \ldots$ as the volumes of permanganate required after intervals of $t_1, t_2, t_3 \ldots$ minutes, the values of K were calculated in accordance with each of the following equations:—

1. $K = \frac{1}{t_2 - t_1} \cdot \log \frac{C_1}{C_2} = \frac{1}{t_3 - t_2} \cdot \log \frac{C_2}{C_3}$, &c., for a reaction of the first order.

2. $K = \frac{1}{t_2 - t_1} \cdot \frac{C_1 - C_2}{C_1 C_2} = \frac{1}{t_3 - t_2} \cdot \frac{C_2 \ C_3}{C_2 C_3}$, &c., for a reaction of the second order.

K (1).	K (2).
0·005877	0·001547
0·004389	0·001558
0·005123	0·001621
0·003980	0·001793
0·005006	0·001675
0·004592	0·001793

The discrepancy between the successive values of K shown in the first column, and the comparative constancy of the values calculated in the second column, appear to indicate a bimolecular reaction.

44. "*Decomposition of Hydrogen Peroxide by Colloidal Platinum.*" By HAROLD LLEWELYN BASSETT.

Bredig investigated the decomposition of hydrogen peroxide by colloidal platinum, and found the change to be unimolecular (Bredig and Müller, *Zeit. Phys. Chem.*, 1900, xxxi., 258). In subsequent discussions of the mechanism of the decomposition, Senter and Sand accept Bredig's result as to the order of the reaction, and the point seems to have been assumed to be finally settled (*Proc. Roy. Soc.*, 1904, lxxiv., 356, 566). The experiments were repeated by Miss Dyer and Miss Dale (see preceding abstract), but it was noticed that very poor unimolecular constants were usually obtained, and the results often corresponded more closely with a bimolecular change.

It appeared of interest to investigate the cause of these apparent anomalies, and it was found that the order of the reaction depends entirely on the concentration of the hydrogen peroxide. Bredig and others worked with solutions of about 1/50 grm.-molecular weight per litre, or even greater dilution than this, and at these dilutions the decomposition certainly is unimolecular. On increasing the concentration, however, the reaction slowly becomes bimolecular, and bimolecular constants are obtained at a concentration of about 1/9 grm.-molecular weight per litre. After this, increase of concentration does not affect the order of the reaction, but owing to the rapid evolution of oxygen the experimental difficulties in obtaining constants become very great.

Nernst suggests that in such cases as these the velocity measured is not that of the chemical change, but simply that of the diffusion of the solute to the surface of the particles of colloidal metal. He assumes that equilibrium is at once set up when this surface is reached.

Senter and Sand discuss this hypothesis and the importance of the part played by convection in the liquid. Their results suggest that the hypothesis, if at all true, will have to be considerably modified to account for the observed values for the velocity constants. It is assumed all through these papers that decomposition of the hydrogen peroxide actually takes place when the molecules come into contact with the surface of the platinum.

This would account for the action being unimolecular, but it is difficult to see how a bimolecular change can be explained in this way. A single molecule would break up when it reached the surface of the platinum, and this decomposition would have no connection with that of other molecules.

To account for the bimolecular change in stronger solutions it is now suggested that, as the concentration increases, hydrogen peroxide molecules meet in the film of solute surrounding the platinum particles without ever reaching the surface of the platinum, and are decomposed in this surface film by contact with one another, possibly owing to the influence of surface tension.

The opportunity for this would clearly be greater in stronger solutions, and with steadily increasing concentration it would gradually become the more important decomposition. Finally, in solutions giving a bimolecular constant, it is practically the only one taking place. Further increase of concentration, whilst increasing the amount decomposed, would have no effect on the order of the reaction, in agreement with experiment. The bimolecular decomposition depends on the presence of at least two hydrogen peroxide molecules in a given small

space at the same time, and this will clearly depend only on the concentration of the hydrogen peroxide, and will not be affected by the amount of platinum present.

This view as to the change in the character of the decomposition with increase of concentration appears to explain satisfactorily all the experimental facts observed.

In carrying out the experiments slightly acid hydrogen peroxide was used, the presence of acid having been shown by Bredig not to affect the course of the decomposition. Solutions of the various strengths were made up and placed in a thermostat at 25°. When the solutions had reached the temperature of the bath, 2 cc. of colloidal platinum solution were added to 100 cc. of the hydrogen peroxide solution. These proportions were used in all the experiments.

Titrations were made on 5 or 10 cc. of the solution at intervals of five or ten minutes, according to the strength of the hydrogen peroxide. Potassium permanganate was used of strengths to give convenient titrations in the various cases. An attempt was made to estimate the hydrogen peroxide by potassium iodide in excess of sulphuric acid, but it was unsuccessful owing to the length of time required to complete the reaction with the hydriodic acid. With the stronger hydrogen peroxide solutions, great difficulty was experienced owing to the rapid evolution of bubbles of oxygen in the pipette, making accurate measurement very difficult.

The figures at the heads of the columns below give the strengths of the hydrogen peroxide in grm.-molecules per litre.

The constants are calculated with ordinary logarithms as their actual magnitudes are not discussed, and as different strengths of permanganate were used the bimolecular-constant values are not comparable, and are only to be considered as regards their constants.

Unimolecular Constants.

0·0034.	0·0141.	0·0208.	0·107.	0·119.	0·145.	0·205.
0·014	0·022	0·021	0·013	0·0043	0·0075	0·0083
0·016	0·024	0·023	0·012	0·0041	0·0068	0·0066
0·015	0·022	0·020	0·011	0·0040	0·0062	0·0072
0·013	0·019	0·018	0·010	0·0032	0·0057	0·0071
0·015	0·017	0·017	0·008	0·0036	0·0051	0·0053
0·015	0·015	0·015	0·008	0·0035	0·0054	0·0057

Bimolecular Constants.

0·0034.	0·0141.	0·0208.	0·107.	0·119.	0·145.	0·205.
0·0036	0·0029	0·0027	0·0016	0·0050	0·0015	0·0012
0·0047	0·0042	0·0038	0·0019	0·0049	0·0015	0·0011
0·0048	0·0049	0·0042	0·0022	0·0051	0·0015	0·0013
0·0052	0·0057	0·0048	0·0021	0·0046	0·0015	0·0013
0·0073	0·0061	0·0056	0·0020	0·0046	0·0014	0·0011
0·0090	0·0082	0·0058	0·0023	0·0050	0·0016	0·0012

(To be continued).

INSTITUTE OF CHEMISTRY.

The Thirty-fifth Annual General Meeting of the Institute of Chemistry was held at 30, Bloomsbury Square on Monday, March 3rd, Prof. Raphael Meldola, D.Sc., F.R.S., President, in the Chair.

Mr. A. Gordon Salamon, Honorary Treasurer, in moving the adoption of the Annual Accounts and the Report of the Auditors, indicated that the Council in their endeavour to develop the work of the Institute were obliged to spend money. One of the chief items of additional expense during the past year had been that incurred in the delivery and publication of lectures; but such expenses were, in his opinion, fully justified and for the good of the Institute. Fortunately the number of candidates for the Examinations during the past year constituted a record, and the number of members had increased by 45, so that in the absence of any abnormal development in expenditure the present year should show a more satisfactory result from the financial point of view. The Institute was to be congratulated on the substantial advance made with the Buildings Fund, but as the preparation of the plans progressed it was becoming more obvious that a very determined effort would have to be made to reach a total of about £16,000, the amount at present promised being £11,014.

Mr. Chaston Chapman seconded, and a cordial vote of thanks was passed to the Honorary Treasurer as well as to the Honorary Auditors for their services.

Dr. L. T. Thorne replied for the Auditors.

The Report of Council was received and adopted.

Prof. Meldola, in the course of his Presidential Address, remarked that the past year had been one of great activity, and that the Institute was to be congratulated upon the substantial progress made in several directions. In thanking the Members for his election to the Chair, he said that he was glad to have an opportunity of making a confession of a change of view concerning the function of the Institute. At the time of its foundation he was one of those who had felt that no justification could be found for the creation of another corporation of chemists, but the more he had seen of its work the more strongly had he become convinced that the Institute had a public mission to fulfil of precisely the same order of importance as that discharged by any other body of professional men who serve the community. The applications of chemistry in every field of human activity had been steadily increasing, and the importance of professional chemists to the public welfare was becoming more and more recognised. They had not secured that full measure of public recognition to which they were entitled, but in this country all scientific affairs moved but slowly. The consolidation and the elevation of the profession and the maintenance of the status of the chemical practitioner would become more and more determined in the future by the standard of efficiency and of conduct set up by the Fellows and Associates. The most important advance made in the year was the adoption by the Fellows and Associates at an Extraordinary General Meeting convened for that purpose of a scheme for securing a site and erecting a building for new headquarters for the Institute. This had been rendered possible by the raising of a fund, which, although not complete, was considered sufficient to warrant the acquisition of the site. It had been originally estimated that about £15,000 would be required. Of this sum over £11,250 had been promised, £9000 having been actually received. As far as could be gathered, it was possible that a sum of at least £16,000 would be required, so that an endeavour had yet to be made to raise a further £5000. The completion of the scheme cannot but be the most earnest wish of all who have at heart the reputation of this country, whose individual workers have contributed so nobly to the advancement of chemical science. It was hoped to create an establishment worthy of the dignity of the Institute as a professional body and of the service rendered to the community by its members. Mr. John J. Burnet had been appointed as architect, and it was expected that building operations would begin in May. The President then mentioned the names of Fellows who had been specially helpful in raising the Buildings Fund, and also the names of the great City Companies, manufacturing firms, and others which were to be found in the list of contributors. Some of the Companies had expressed their pleasure in having an opportunity of subscribing for the reason that they had received so much advantage from chemical control in their industry, and other similar messages of sympathy and encouragement have been received.

Continuing, the President referred to the recognition accorded to the qualifications of the Institute by Government Departments at home, in the over-seas Dominion, and in India. The Institute had taken its place as an imperial organisation, and it had set before it an ideal for which it was striving. It was hoped that in time every British chemist holding any position of responsibility, whether in the public service, in the teaching profession, in the

chemical factory, or as a private practitioner, would be found on the Register, and that the appearance of a name on that Register should become a necessary public guarantee of efficiency in the same sense that a name on the Medical Register entitled a medical man to practise. It might be long before the whole of this ideal was reached, but the general movement was assuredly in the right direction; while the status of the Institute was recognised as a collective body, it could not be said that the recognition of the members as individuals was satisfactory. This was equally true of the public analyst, the teacher, and the chemical technologist. The question of remuneration was very much a matter of individuality and depended on three factors: the place where the work was done, the actual value of the work to the employer, and the professional status and personal character of the employee. These factors were so variable that it would be as impossible to standardise the value of every particular member as it would be to enforce a particular scale of remuneration for each individual member of any other professional body. It was thought that it might be possible to draw up a schedule of fees for the more routine work which would represent adequate remuneration, and a Committee of the Institute was engaged in this task. If found practicable, the schedule when issued should at any rate serve as a useful guide to members in dealing with clients and public bodies. It might be impossible for the Institute to lay down compulsory regulations as to the fee to be charged, but it would perhaps engender a general understanding among the Members which would make it distinctly known that the services rendered to the community by professional chemists in every department of their work were very much under-estimated. Until the whole level of public appreciation of the value of this profession was raised, the country was destined to lose the services of that highest type of cultured and trained chemist of which other nations are more wisely availing themselves, to our detriment and their advantage. The Institute had sent representatives to give evidence concerning chemists in Government employment before the Royal Commission on the Civil Service. The best thanks of the Institute were due to Sir William Tilden and Sir William Ramsay for their services in this connection, and it was earnestly hoped that some practical amelioration of the existing state of affairs would result. One very important step in the desired direction would be made if the Commissioners could only see their way to adopt the recommendation that Government chemical departments should be controlled by chemists. Turning to the question of the future development of the Institute, the President indicated the desire of the Council to arrange a Conference of Professors of Chemistry to consider the relationship of the qualifications of the Institute to those granted by other educational institutions. Was it not desirable in the interests of the chemical profession, in its broadest sense, that in an understanding with the teaching portion of the profession those who represent the collective body of practitioners should arrive at some concordant scheme of action which should be helpful alike to teaching institutions and to the Institute, and so to the cause of the chemical profession as a united profession in this country? An endeavour should be made to make the interests of the teachers and practitioners identical, and so avoid conflict, wasteful repetition, overlapping, and frittering away of resources which had been the curse of educational development in this country. It was not suggested that the Institute should assume dictatorial powers. The situation had to be faced, and there were many problems which could only be solved by coming to an understanding with the educational authorities, and it certainly appeared that some effort towards standardising the chemical curricula of the country in relation to the examinations of the Institute should be made, or, at any rate, an opportunity given for an exchange of views among the teachers concerned.

On the motion of Mr. David Howard, seconded by Sir William Tilden, a hearty vote of thanks was accorded to the President for his Address.

Mr. L. Myddelton Nash, Mr. W. J. Atkinson Butterfield, and Dr. P. E. Spielmann were appointed Honorary Auditors for the ensuing year.

The ballot having been taken, Dr. George Beilby, F.R.S., Dr. Frank Clowes, Prof. F. P. Frankland, F.R.S., and Mr. David Howard were declared elected as Censors.

The President and Council for the ensuing year were also declared duly elected as nominated.

A vote of thanks was accorded to the retiring officer and Members of Council, on the motion of Mr. W. D, Borland, seconded by Mr. Edward Hinks, and the meeting was dissolved.

The Officers and Council for the ensuing year are as follows:—

President—Raphael Meldola, D.Sc., LL.D., F.R.S.

Vice-Presidents—G. T. Beilby, LL.D., F.R.S.; George McGowan, Ph.D.; Sir Alexander Pedlar, C.I.E., F.R.S.; Sir Boverton Redwood, Bart., D.Sc.; Sir William A. Tilden, D.Sc., LL.D., F.R.S.; E. W. Voelcker, A.R.S.M.

Hon. Treasurer—A G. Salamon, A.R.S.M.

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Royal Institution.—The following are the Lecture Arrangements at the Royal Institution, after Easter:—Dr. A. S. Woodward, two lectures on "Recent Discoveries of Early Man." Prof. W. Bateson, Fullerian Professor of Physiology, two lectures in continuation of his before Easter course on "The Heredity of Sex and some Cognate Problems." Prof. W. Stirling, three lectures on "Recent Physiological Inquiries—(1) Protective and other Reflex Acts; (2) Equilibrium and the Sixth Sense; (3) Ductless Glands and their Dominating Influence." Prof. T. B. Wood, three lectures on "Recent Advances in the Production and Utilisation of Wheat in England." Dr. E. Frankland Armstrong, two lectures on (1) "The Bridge into Life"; (2) "Colour in Flowers." Prof. J. Garstang, three lectures on "The Progress of Hittite Studies—(1) Recent Explorations; (2) Religious Monuments of Asia Minor; (3) Cults of Northern Syria." Mr. Edward Armstrong, two lectures on "Florentine Tragedies—(1) The Exile of Dante; (2) The Burning of Savonarola." Prof. W. J. Pope, three lectures on "Recent Chemical Advances—(1) Molecular Architecture; (2) Chemistry in Space; (3) The Structure of Crystals." Mr. A. M. Hind, two lectures on (1) "Van Dyck and the Great Etchers and Engravers of Portrait"; (2) "Rembrandt's Etchings." Prof. Sir Walter Raleigh, three lectures on (1) "Boccaccio"; (2) "Mediæval French Novelists"; (3) "Chaucer." Mr. H. A. Humphrey, two lectures on "Humphrey Internal Combustion Pumps." Prof. E. Rutherford, three lectures on "Radio-activity—(1) The α-Rays and their connection with the Transformations; (2) The Origin of the β- and γ Rays and the connection between Them; (3) The Radio-active State of the Earth and Atmosphere." The Friday Evening Meetings will be resumed on April 4, when Mr. James J. Dobbie will deliver a discourse on "The Spectroscope in Organic Chemistry." Succeeding discourses will probably be given by Mr. C. J. P. Cave, Dr. T. M. Lowry, Prof. J. Garstang, Mr. H. G. Plimmer, and other gentlemen.

NOTICES OF BOOKS.

An Introduction to Mathematical Physics. By R. A. Houstoun, M.A., Ph.D., D.Sc. London, New York, Bombay, and Calcutta: Longmans, Green, and Co. 1912.

This book contains a course of lectures given by the author to the Natural Philosophy Class A at the University of Glasgow, and will be found a valuable introduction to the study of more advanced treatises in some branches of mathematical physics. The author assumes his readers to possess a thorough knowledge of elementary dynamics and physics, and also to be fairly proficient in all the ordinary operations of the calculus. It seems probable that the average student, unless his mathematical training had been very thorough, would require some help in following the text, and the problems, many of which are taken from papers set at Glasgow University Examinations, are in some cases decidedly difficult.

Mixed Metals or Metallic Alloys. By Arthur A. H. Hiorns. Third Edition. London: Macmillan and Co., Ltd. 1912.

A good descriptive account of all the most important alloys is to be found in this book, which will be a useful guide for manufacturers and students. An introduction deals with the elementary chemistry of both the metals and non-metals, and general methods of preparing alloys and their chief properties are then described. Subsequently the individual alloys are treated in detail. In the third edition many new alloys are described for the first time, and the latest data and statistics obtainable are given. Much attention is paid to the uses to which the various alloys are put, and their practical applications are fully treated.

The Principles and Practice of Textile Printing. By Edmund Knecht, Ph.D (Zurich), M.Sc.Tech. (Manchester), F.I.C., and James Best Fothergill. London: Charles Griffin and Co., Ltd. 1912.

In recent years many changes have been made both in the methods employed in calico printing and in the materials used. Whole classes of new colouring matters have been discovered and have found wide application, while the prices, formerly prohibitive, of other dyes have diminished to such an extent that they can be freely used for all kinds of materials. Hence a want has been felt for a text-book devoted exclusively to modern practice, and the authors are particularly well qualified to supply it. They have succeeded in giving an impartial view of different classes of dyes, and have discussed in detail methods of printing, preparing for printing, &c. A great number of formulæ for dyes are given, and printed patterns of the actual stuffs are frequently inserted in the text to illustrate the effects obtained. A price list of drugs is included among the addenda, and the authors, by keeping strictly within the limits of their subject and not discussing such matters relating to the composition and character of dyes as are to be found in their "Manual of Dyeing," have been able to give their readers a really comprehensive account of textile printing.

Electroplating. By William R. Barclay, A.M.I.E.E., and Cecil H. Hainsworth, A.M.I.E.E. London: Edward Arnold. 1912.

This book has been written for the enlightened practical man, who is not content to work by rule-of-thumb methods, but who wants some scientific knowledge upon which to base his practice. For such it is a thoroughly useful guide. Short sketches are first given of the principles of chemistry, electrochemistry, and electricity which should be known to the reader. These accounts are necessarily only slight, but the smallness of the space that can be given to them precludes the possibility of anything like a full treatment. The elements of electricity are well explained in clear language, and some examples of simple calculations are given. Following on these introductory chapters details are given of methods of deposition of all the common metals. Formulæ of solutions actually in use in workshops and not merely for laboratory purposes are given, and some methods which are of perhaps more academic than practical interest are included. The book deserves to be widely used in technical schools and colleges, as well as in electroplating works, and can be recommended as likely to be found thoroughly practical and reliable.

The Chemistry of Anæsthetics. IV. *Chloroform.* By Charles Baskerville and W. A. Hamor.

This paper has been reprinted from the *Journal of Industrial and Engineering Chemistry*, and gives a very exhaustive account of the manufacture, purification, and decomposition of chloroform. The results of the determination of its physical constants are tabulated, and the impurities of anæsthetic chloroform are fully discussed. Methods of testing it are also treated, and a scheme is given for its systematic examination. The innumerable footnotes and references make the paper somewhat tiresome to read, but the subject is certainly treated with great completeness.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Heddomadaires des Séances de l'Académie des Sciences. Vol. clv., No. 26, December 23, 1912.

Detection and Estimation of Free Yellow Phosphorus in Phosphorus Sesquisulphide.—Th. Schlœsing.—The employment of solvents to determine free phosphorus in phosphorus sesquisulphide has been regarded as useless, for if a good solvent for phosphorus, such as carbon disulphide, is employed it also dissolves the sesquisulphide. But if a less efficient solvent is employed, by suitably varying the conditions it will be possible to dissolve out all the phosphorus and only a little of the sesquisulphide, and by evaporation the proportion of yellow phosphorus will be increased. A suitable solvent is rectified petroleum ether.

Properties of Alkaline Nitrites.—Marcel Oswald.—Ordinary commercial sodium nitrite contains about 90 per cent of nitrite, the residue being sulphate, nitrate, and chloride of sodium, and a little sand. The pure salt can be obtained by three or four crystallisations by the rapid cooling of the hot saturated solution. The nitrites of potassium, lithium, and the alkaline earth metals can be obtained from it by double decomposition. The sodium salt is white, unaltered in air at 120°, and not hygroscopic. The potassium salt is yellowish and very deliquescent. The melting-points are 217° for $NaNO_2$ and 297·5° for KNO_2, and the densities 2·168 for $NaNO_2$ and 1·912 for KNO_2.

Atomic Weight of Uranium.—Oechsner de Coninck.—When anhydrous uranyl oxalate, $C_2O_4UO_2$, is heated in absence of air it splits up into UO_2 and CO_2. It can be obtained in a very pure state by the action of a saturated solution of oxalic acid on a dilute solution of pure uranyl nitrate. If p is the weight of the dry oxalate and p' the weight of UO_2 obtained, the molecular weight of UO_2 can be calculated from the equation $p/p' = x + 88/x$. The mean value obtained in seven experiments was 270·40, which gives 238·4 for the atomic weight of uranium.

Action of Hydrogen Peroxide on Oxythionaphthene, Oxythionaphthene Carbonic Acid, and Thioindigo.—Maurice Lanfry.—When hydrogen peroxide

acts on oxythionaphthene the phenolic hydroxyl remains unaltered, and the two new oxygen atoms attach themselves to the sulphur. Thus an S dioxy-oxy-3-thionaphthene is formed. A small quantity of sulphuric acid is also formed at the expense of the thiophenic sulphur. The sodium salt of oxythionaphthene carbonic acid is almost entirely resinified by the action of H_2O_2, and a small amount of thioindigo is also formed. Hydrogen peroxide acts on thioindigo only when it is very finely divided.

Bromination of Cyclopentanone.—Marcel Godchot and Félix Taboury.—When bromine dissolved in carbon tetrachloride is added to a solution of cyclopentanone in the same solvent, and a rise of temperature is prevented by a current of cold water, crystals of tetrabromocyclopentanone, $C_5H_4OBr_4$, separate. If a concentrated solution of the tetrabrom compound in acetic ether is allowed to stand, HBr is given off, and crystals of tribromocyclopentenone, $C_5H_3OBr_3$, are deposited. The addition of the corresponding quantity of bromine to a solution of the last substance gives pentabromocyclopentanone, $C_5H_3OBr_5$.

Nitro Derivatives of Metacresyl Oxide.—A. Mailhe.—If metacresyl oxide is nitrated in an acetic medium and the temperature is allowed to rise to 80° or 90°, a black viscous mass is obtained, from which the dinitro compound $C_6H_3(NO_2)(CH_3)—O—C_6H_3(CH_3)(NO_2)$ can be separated. When the nitration of metacresyl oxide is performed by means of fuming nitric acid, the tetranitro derivative is obtained. Further nitration cannot be effected.

Bulletin de la Société Chimique de France.
Vol. xi.-xii., No. 24, 1912.

Isomorphism in the Organo-Mettalic Series.—Paul Pascal.—The thermic study of the sulphide, selenide, and telluride of phenyl shows that these substances are isomorphic in pairs, and confirms the fact that sulphur and selenium are more closely related.

Oxides of Uranium.—Oechsner de Coninck and A. Reynaud.—The authors placed some uranium formate and methanol in a flask and exposed it to diffused light for three months. They thus obtained a brown homogeneous mass consisting of uranous oxide. Apparently the formate first reacts with 1 molecule of water of crystallisation:—

$$\begin{matrix}CHO.O\\CHO.O\end{matrix}>UO_2 + H_2O = UO_3 + 2(CHO.OH).$$

The uranic hydride thus formed is reduced to uranous oxide: $CH_2O + UO_3 = UO_2 + CH_2O_2$. When uranous oxide is heated in air it absorbs oxygen and gives rise to U_4O_{10}, which is peruranic anhydride, $U_4O_{10} = 2(U_2O_5)$.

Determination of Phosphorus in Lecithine.—P. Freundler.—Two or three grms. of lecithine are heated with 50 cc. of fuming nitric acid for two or three hours. Then 25—35 grms. of permanganate are added in small quantities, and when the oxidation is completed the liquid is diluted to 150—200 cc., the manganese dioxide precipitated is dissolved by means of concentrated sodium nitrate and the solution is concentrated. The syrup obtained is taken up with 60—80 cc. of water and precipitated with molybdic reagent without previous filtration. The estimation is then proceeded with in the usual way.

MISCELLANEOUS.

Royal Institution.—A General Meeting of the Members of the Royal Institution was held on the 3rd inst., Sir James Crichton-Browne, Treasurer and Vice-President, in the Chair. Mr. T. W. E. Davenall, Mr. P. M. Deneke, Mr. H. Trevelyn George, Mr. H. G. Gillespie, Mr. W. V. Graham, Lady Heath, the Hon. Marguerite de Fontaine Drever Joicey, Mr. J. A. Law, Rev. J. Marchant, Dr. W. A. Milligan, Mr. D. W. Moncur, the Hon. Mrs. R. Parker, Mrs. Carson Roberts, and Miss Tatlock were elected Members. The Honorary Secretary announced the decease of the Right Hon. the Earl of Crawford, Mr. George Matthey, and Sir William H. White, Members of the Royal Institution, and Resolutions of condolence with the relatives were passed.

Colloids and their Viscosity.—The next meeting of the Faraday Society will take the form of a General Discussion on "Colloids and their Viscosity," and will take place on Wednesday, March 12, in the rooms of the Chemical Society, Burlington House, Piccadilly, London, W. The meeting will be open to Fellows of the Chemical Society, and members of the Society of Chemical Industry, the Institution of Electrical Engineers, and the Physical Society of London. Others interested in the subject desirous of being present should apply to the Secretary of the Faraday Society, 82, Victoria Street, London, S.W. The President, Dr. R. T. Glazebrook, C.B., F.R.S., will preside over the Discussion. The following provisional programme has been arranged:—

Tea will be served at 4 p.m. before the meeting.

4.30—6.0 p.m., the following papers will be read:—

Dr. Wolfgang Ostwald (Leipzig)—"On the Bearing of Viscosity on the Study of the Colloidal State."

Prof. Victor Henri (Paris)—"The Determination of the Size of Colloid Particles and the Relation of the Size with the Viscosity of Disperse Systems."

Prof. Dr. W. Pauli (Vienna)—"Viscosity and the Electro chemistry of Protein Solutions."

Prof. Dr. H. Freundlich and Dr. N. Tshizake (Brunswick)—"On the Rate of Coagulation of $Al(HO)_3$ Solution as Measured by Change in Viscosity."

At 6.0 p.m. the meeting will adjourn for dinner at the Trocadero Restaurant.

The Discussion will be resumed at 8.0 p.m., when—

Mr. Emil Hatschek will read a paper on "The Mathematical Theory of the Viscosity of 2-Phase Systems."

Prof. F. G. Donnan, F.R.S., will speak on "The Viscosity of Soap Solutions."

Dr. S. B. Schryver will speak on "The Relation of Viscosity to Solubility."

Prof. W. Nernst, Prof. W. M. Bayliss, F.R.S., and Prof. W. B. Hardy, F.R.S., will also take part in the Discussion.

The subject will then be open for General Discussion.

MEETINGS FOR THE WEEK.

Monday, 10th.—Royal Society of Arts, 8. (Cantor Lecture). "Coal Gas as a Fuel for Domestic Purposes," by Francis W. Goodenough.

Tuesday, 11th.—Royal Institution, 3. "The Movements of the Stars," by Prof H. H. Turner, D.Sc., F.R.S.

—— Royal Sanitary Institute, 7.30. Discussion on "Milk and Dairies Bill."

Wednesday, 12th.—Royal Society of Arts, 8. "The Use of White Lead in Painting," by Noel Heaton, B.Sc.

Thursday, 13th.—Royal Institution, 3. "Surface Energy," by W. B. Hardy, F.R.S., &c.

—— Royal Society. "A Simple Method of finding the Approximate Period of Stable Systems," by A. Mallock. "Motion of Electrons in Gases," by J. S. Townsend and H. T. Tizard. "The Self-inductance of Circular Coils of Rectangular Section," by T. R. Lyle. "Ammonium Ferrous Sulphate and its Alkali-metal Isomorphs," by A. E. H. Tutton. "Re-combination of the Ions produced by Röntgen Rays in Gases and Vapours," by H. Thirkill. "Optical Investigation of Solidified Gases—III., The Crystal Properties of Chlorine and Bromine," by W. Wahl

Friday, 14th.—Royal Institution, 9. "Great Advance in Crystallography," by A. E. H. Tutton, F.R.S., &c.

—— Physical Society, 5. "Some Oscillograms of Condenser Discharges and a Simple Theory of Coupled Circuits" and Exhibition of Braun Cathode Ray Tubes and an Electrostatic Machine for working them, used as a High-frequency Oscillograph, by J. A. Fleming. "Stretching and Breaking of Sodium and Potassium" (with Demonstrations), by B. B. Baker. "Latent Heat of Evaporation of Aqueous Salt Solutions," by R. G. Lunnor. "Some Flame Spectra" (with Demonstrations), by E. N. da C. Andrade. Demonstration of Spark Photograph by W. B. Haines.

Saturday, 15th.—Royal Institution, 3. "The Properties and Constitution of the Atom." by Prof. Sir J. J. Thomson, O.M., F.R.S., &c.

THE CHEMICAL NEWS.

Vol. CVII., No. 2781.

DETERMINATION OF COPPER IN WHITE METAL ALLOYS.

By F. IBBOTSON and L. AITCHISON.

Type-metal, bearing metals, Brittania metal, and similar alloys containing tin, lead, and antimony in varying proportions generally contain also a few per cents of copper. The separation and determination of this element by any of the ordinary methods of analysis is a matter of some considerable difficulty and occupies much time, and generally involves the use of sulphuretted hydrogen.

The authors have previously stated in this journal that they have succeeded in separating copper from tin, when they occur together in the approximate proportion of nine to one, by means of hydrazine hydrochloride. Jannasch and Biedermann (*Ber.*, 1900, 631) have shown that copper may be separated from zinc and arsenic by means of hydrazine sulphate and excess of sodium hydrate. Cuprous oxide is first precipitated, but is replaced on digestion by metallic copper. In the case of the separation of copper from tin, they found that sulphates impaired the accuracy of the separation, as small quantities of tin invariably accompanied the metallic copper and could not be removed by washing with dilute sodium hydrate solution. Much better results were obtained when the hydrochloride was substituted for the sulphate, and Jannasch and Biedermann quote figures from which it is seen that an accurate separation of as much as 75 parts of copper from 25 of tin can be made. They use approximately 0·25 grm. of the mixed metals, and 15 times that amount of sodium hydrate along with 2 to 3 grms. of hydrazine hydrochloride.

Since salts of lead yield no precipitate with a large excess of sodium hydrate, as also salts of antimony in the presence of tartrates, the authors have applied the method described under the "Determination of Tin in Bronzes" in this journal to the determination of copper in white metal alloys. As in the case of commercial bronzes, so also here it was found that if the amount of sodium hydrate was increased to 40 times that of the alloy taken, the separation of copper from the other elements was complete in all cases, provided that the solution of the mixed metals was allowed to run in drops into the hot, agitated mixture of soda and hydrazine hydrochloride.

They therefore recommend the following method, which can be executed in from two to two-and-a-half hours, for the determination of copper in any kind of white alloy.

0·5 grm. of the drillings or filings are dissolved in 10 to 15 cc. aqua regia, water added in equal volume and the solution cooled. Should there be a separation of crystals of lead chloride, the latter are strained off through a small paper pulp filter, washing with cold water. To the solution about one grm. of tartaric acid is added, and when this dissolves a solution of sodium hydrate is added until the acids are neutralised or nearly so. The mixture is then heated to boiling, and, by means of a separating funnel, allowed to run in drops into a solution, also boiling, of 20 grms. of sodium hydrate and 2 to 3 grms. of hydrazine hydrochloride in 250 to 300 cc. of water. The latter solution is vigorously agitated during the operation. The precipitate of metallic copper is filtered through ashless paper pulp, after digesting the mixture for about fifteen minutes. After washing with hot water, the metal is dissolved from the filter in a mixture of equal parts of nitric acid (1·20) and water, the filter well washed, and the solution so obtained evaporated to pastiness. On taking up in water and a few drops of nitric acid, it should be free from any opalescence or precipitate, which would be caused by the presence of a small quantity of unseparated stannic oxide, neither should the ignition of the pulp filter yield anything more than the negligible amount of ash. Sodium carbonate solution is next added to the solution containing the copper until it is alkaline, then acetic acid in slight excess, and the solution boiled. After cooling, the copper is determined iodometrically by adding about one grm. of potassium iodide, and titrating with a weak standard solution of sodium thiosulphate and the usual starch indicator. As white metal alloys rarely contain more than 5 per cent of copper, the authors use a solution of thiosulphate, 1 cc. of which represents 1 mgm. of copper.

The authors have tested the above method on alloys containing as much as 80 per cent of lead, together with tin and antimony, and also on alloys containing the same amount of tin together with lead and antimony. The small quantities of zinc which occur in these alloys are also completely separated from copper, and the minute quantities of iron which occur as unavoidable impurities in white metals are without appreciable effect on the results.

Metallurgical Department,
University of Sheffield.

THE ESTIMATION OF TITANIUM IN THE PRESENCE OF IRON.

By WILLIAM M. THORNTON, Jun.

During the author's service as chemist on the Virginia Geological Survey a good many titaniferous rocks, containing the minerals rutile and ilmenite in various associations, were presented for analysis. Since the titanium content of these rocks are often high (amounting to 69 per cent in a few cases) it was necessary to resort to a reliable gravimetric method. Among the gravimetric methods in use at the present time that have been thoroughly tested, the one brought out by Gooch (*Proc. Am. Acad. Arts and Sci.*, New Series, xii., 435) is perhaps unequalled, and especially recommends itself because the iron can be completely separated from the titanium by a single treatment. This method provides not only for the separation of titanium from iron but also from aluminium and phosphoric acid. Since the Virginia rocks which ran highest in titanium were non-aluminous (or nearly so), it occurred to the author that the method might be so modified as to shorten the process and eliminate some of the more difficult manipulation.

The first step is to separate the iron. This is done by adding tartaric acid in quantity equal to three times the aggregate weight of the oxides to be held by it in solution. Hydrogen sulphide is then introduced until the iron has been reduced to the ferrous condition. Ammonium hydroxide is then added to slight alkalinity, and hydrogen sulphide again passed in until the iron has been completely precipitated, and the solution left faintly alkaline to litmus-paper. After filtration and washing of the ferrous sulphide with very dilute colourless ammonium sulphide, the titanium is entirely in the iron-free filtrate. The tartaric acid must next be destroyed; for titanium cannot be precipitated by any reagent in its presence. This is done by acidifying the filtrate with considerable sulphuric acid, boiling out the hydrogen sulphide thus set free, and adding potassium permanganate (in the form of a strong solution) to the boiling solution until a permanent precipitate of manganic hydroxide appears, which is dissolved in a little sulphurous acid. The result of this reaction is that the tartaric acid is oxidised partly to formic acid and partly to carbonic acid. The titanium can then be precipitated by the basic acetate process. Much manganese is thus introduced into the solution, and is co-precipitated in some

measure with the titanium - necessitating a solution of the precipitate, and a second precipitation of the titanium by the above mentioned process. This makes no difference when the amount of aluminium is relatively large; for, although titanium can be completely thrown down in a solution containing up to 11 per cent of absolute acetic acid and thereby separated from most of the aluminium (not from all of it), at least a second precipitation is required.

It seemed probable to the author that some oxidising agent could be found by means of which the tartaric acid could be broken down and at the same time introduce no substance that would contaminate the titanic acid; so that in cases where the aluminium was small in amount relative to the titanium one precipitation would suffice. After several unsuccessful experiments with different oxidising agents, the plan of using a mixture of sulphuric acid and fuming nitric acid was tried with very gratifying results.

Two standard solutions containing titanic sulphate were employed in the following experiments:- The first was prepared by fusing Merck's titanium dioxide with sodium pyrosulphate, extracting the melt with 10 per cent sulphuric acid, filtering, and making up to a definite volume. The second was prepared by treating twice crystallised potassium fluotitanate with concentrated sulphuric acid—the sulphuric acid being kept at the fuming-point for several hours, poured into cold water, and filtered. In either case the solution contained about 10 per cent of absolute sulphuric acid. Duplicate portions of 25 cc. each were taken for standardisation. Ammonium hydroxide was added until the solution was nearly neutral (the approach to neutrality being determined by the formation of a turbidity which disappeared but slowly after vigorous stirring). About 1 cc. of a strong solution of ammonium bisulphite was added as a precaution to prevent the precipitation of any iron that might accidentally have found its way into the solution. Five 5 cc. of glacial acetic acid and 15 grms. of ammonium acetate were also added, and the volume was made up to about 350 cc. The solution was then brought rapidly to boiling, and maintained in ebullition for about two minutes. The titanium came down in flocculent and readily filterable condition. The precipitate was washed first with water containing acetic acid, and finally with pure water. Ignition in contact with the paper was performed in the usual manner, and finally the heat of a Meker burner was applied for twenty minutes. Duplicate determinations agreed to within 0·0001 grm.

The first series of experiments were carried out with a view to determining whether or not the titanium could be completely recovered after destruction of the tartaric acid in a solution containing the same constituents as the acidified and boiled filtrate from the ferrous sulphide in an actual separation. Accordingly, to a 25 cc. portion of the standard titanic sulphate solution exactly three times the weight of the titanium dioxide in tartaric acid was added, followed by ammonium hydroxide to alkalinity, and then 10 to 12 cc. of concentrated sulphuric acid. The solution was then evaporated down to incipient charring of the tartaric acid. The basin was then covered with a watch-glass, and the heating continued till further charring and frothing had taken place, as much as the capacity of the vessel would permit. (A 200 cc. platinum basin of the Blair type was found to be the most satisfactory for the purpose). After cooling a little, 5 cc. of fuming nitric acid were added through the lip opening with a pipette. After the first violence of the reaction was over cautious heating was applied. A vigorous reaction took place accompanied by much effervescence and copious evolution of brown fumes. The organic matter gradually disappeared. The effervescence became steady, finally ceased, and the sulphuric acid began to fume. A pale yellow syrupy liquid resulted. The liquid was poured into 100 cc. of cold water, and after filtration the titanium precipitated exactly as described under standardisation. Table I. shows the results of five experiments carried out in the above manner.

TABLE I.—*The Recovery of Titanium after Oxidation of Tartaric Acid by Sulphuric Acid and Fuming Nitric Acid.*

No.	Titanic sulphate = by standardisation TiO_2.		Found TiO_2.	Error.	Alkali salt.
	Cc.	Grm.	Grm.	Grm.	
1.	25	0·1012	0·1015	+0·0003	$HNaSO_4$
2.	25	0·1012	0·1013	+0·0001	$HNaSO_4$
3.	25	0·1256	0·1264	+0·0008	$HKSO_4$
4.	25	0·1256	0·1256	—	$HKSO_4$
5.	25	0·1256	0·1259	+0·0003	$HKSO_4$

A solution of ferric sulphate was prepared by dissolving ferric ammonium alum in water, and adding a little sulphuric acid to prevent the formation of basic salt. The solution was standardised by potassium permanganate which had previously been standardised against sodium oxalate.

In the second series of experiments actual separations of titanium from iron were carried out in the manner detailed in the introduction. The filtrate from the ferrous sulphide was acidified with 12 cc. to 15 cc. of concentrated sulphuric acid, and after evaporation down to a small bulk was transferred to a 200 cc. deep form basin, evaporated further, and the tartaric acid destroyed by the method above given. Table II. shows the results of seven experiments.

TABLE II.—*The Separation of Titanium from Iron.*

No.	Ferric ammonium sulphate = Fe_2O_3.		Titanic sulphate = by standardisation TiO_2.		Found. TiO_2.	Error.	Alkali. salt.
	Cc.	Grm.	Cc.	Grm.	Grm.	Grm.	
1.	20	0·1430	25	0·1012	1·1018	+0·0006	$NaHSO_4$
2.	20	0·1430	25	0·1012	0·1016	+0·0004	$NaHSO_4$
3.	20	0·1430	25	0·1012	0·1015	+0·0003	$NaHSO_4$
4.	20	0·1430	25	0·1012	0·1013	+0·0001	$NaHSO_4$
5.	20	0·1430	25	0·1012	0·1012	—	$NaHSO_4$
6.	20	0·1430	25	0·1256	0·1258	+0·0002	$KHSO_4$
7.	20	0·1430	25	0·1256	0·1259	+0·0003	$KHSO_4$

A method has been satisfactorily worked out for the separation of titanium from iron and destruction of the tartaric acid, of such a nature as to introduce no foreign substance that will contaminate the titanium when subsequently thrown down. Except for the evaporation of the filtrate from the ferrous sulphide, the operations can be quickly performed. Evaporation, however, is an operation which does not demand the analyst's constant attention.—*American Journal of Science*, xxxiv., p. 214.

A GENERAL METHOD FOR THE PREPARATION OF THE AMMONIUM SALTS OF ORGANIC ACIDS.

By EDWARD H. KEISER and L. McMASTER.

THE usual method of preparing the ammonium salts of organic acids, namely, neutralising the aqueous solution of the acid with ammonia, and evaporating to crystallisation, gives very unsatisfactory results owing to the hydrolytic action of water upon these salts. A study of the literature of ammonium salts of organic acids shows that comparatively few of them have been made and analysed. In the case of dibasic acids usually only the acid ammonium salt has been prepared.

In attempting to prepare the amide of maleic acid we desired to start with the diammonium maleate, but found it impossible to make this salt by neutralising a solution of maleic acid with ammonia and evaporating to crystallisation. We therefore dissolved the acid in ether, and conducted a stream of dry ammonia gas into the ethereal solution. A white flocculent rather gelatinous precipitate at first formed; this soon collected into lumps, and, on

continuing to pass in ammonia, changed into a white crystalline powder. Analysis showed it to be diammonium maleate.

This method of preparing diammonium maleate was found to be applicable, in a general way, to the preparation of the ammonium salts of other organic acids. In those cases in which the acid was insoluble in ether some other solvent, such as absolute alcohol, or a mixture of ether and alcohol, was used. The method is dependent upon the fact that most organic acids are soluble in ether or alcohol, or a mixture of the two, while the ammonium salts are insoluble, and can be thrown down by means of a stream of dry ammonia gas. Very good yields are obtained by this method. The organic salts of other weak bases, such as the salts of aniline, the amines, and other organic bases, can, no doubt, be made in the same general way by doing away with aqueous solutions, and using only alcoholic or ethereal solutions of both acid and base.

We have made, in this way, the ammonium salts of maleic, fumaric, mesaconic, citraconic, malonic, and phthalic acids.

Ammonium Maleate.—This salt was precipitated from the ethereal solution of the acid by a stream of dry ammonia, as described above, washed on the filter with ether, and dried in the air. It is a white crystalline powder, not deliquescent in the air but readily soluble in water. Büchner (*Liebig's Ann. Chem.*, xlix., 67) describes this salt as being deliquescent, but his compound was prepared in the wet way. This salt has an odour similar to that of acetamide. Analyses gave the following results :—

	C.	H.	N.
Calculated for $C_2H_2(CO_2NH_4)_2$	31·97	6·71	18·66
Found—I.	—	—	16·12
II.	31·20	7·09	16·13
III.	32·04	6·89	18·70
IV.	32·06	6·91	18·46

The first two nitrogen determinations were made by the Kjeldahl method and gave low results, the last two by the Dumas method. We also prepared this salt by precipitation with ammonia in a solution of the acid in absolute alcohol.

Ammonium Fumarate.—Fumaric acid was dissolved in absolute alcohol and dry ammonia conducted into the solution. A heavy white amorphous powder was at once formed. It was filtered, washed thoroughly with alcohol and ether, and dried in air on a porous plate. This salt has no odour, as in the case of the diammonium maleate. It is not deliquescent but dissolves readily in water. It gave, on analysis, the following results :—

	N.
Calculated for $C_2H_2(CO_2NH_4)_2$	18·66
Found—I.	18·47
II.	18·50

Ammonium Mesaconate.—The mesaconic acid, obtained from Kahlbaum, was dissolved in ether and dry ammonia conducted into the solution. A gelatinous precipitate was at first formed, but this soon changed into a crystalline powder. The salt was filtered, washed on the filter with ether, and then dried in the air. Like the ammonium fumarate, it had no odour. It was not deliquescent, but dissolved readily in water. Determinations of nitrogen gave the following results :—

	N.
Calculated for $CH_3C_2H(CO_2NH_4)_2$ ..	17·07
Found—I.	16·71
II.	16·84

Ammonium Citraconate.—Citraconic acid (Kahlbaum) was dissolved in ether, and ammonia passed into the solution. A thick colloidal solution was at first formed, but as the ammonia continued to pass into the solution this changed into a crystalline precipitate. This was filtered, washed with ether, and dried in the air. Like the ammonium maleate it has an odour like that of acetamide. The salt is not deliquescent, but soluble in water.

	N.
Calculated for $CH_3C_2H(CO_2NH_4)_2$ ..	17·07
Found—I.	16·82
II.	16·87

The ammonium salts of malonic and phthalic acids were also made by the same general method. The ammonium malonate came down in ether solution as a fine white crystalline precipitate. It had no odour, and was not deliquescent, although readily soluble in water. The ammonium phthalate was obtained as a white powder.—*American Chemical Journal*, xlix., No. 2.

FREE LIME IN PORTLAND CEMENT.*

By H. E. KIEFER.

It is to be regretted that the majority of chemists engaged in the manufacture of Portland cement have very little time for research work. Some of us have considerable time for experimental work, but the time and money spent are expected to produce commercial results rather than contribute to the stock of purely scientific knowledge. This latter we are compelled to leave to the research chemist, and as he usually lacks a practical manufacturing experience we may be able to supply a few facts and suggestions.

One of the most troublesome arguments which the cement chemist has to meet is on the subject of *Free Lime*. We hear it discussed by chemists and engineers and attribute all kinds of defects in the cement to it, yet it is very questionable whether any of us have a well-grounded theory for the position we assume. We manufacture a product to meet certain specifications, and when it fails in any of these we look for the cause and a remedy from a practical rather than a theoretical point of view, using theory only to facilitate results. A few things we know and many more we believe, hence we shall state first the general knowledge and follow it up with the theory and then add a few observations which may furnish suggestions for research chemists.

Constancy of volume is one of the requirements of practically all specifications. The test is made by subjecting a hardened pat to five hours' boiling in water in a loosely covered vessel or to the steam above the water in such a vessel. If the pat comes out sound and hard, with no signs of warping, checking, or disintegration, the cement is considered sound. On the other hand, if it becomes soft, or warps or cracks on the edges, it is considered unsound. From this point the theory begins. The explanation is that a failure to pass the test is due to free lime. Various quantitative methods have been suggested with a view of determining it, but so far as the writer knows none has ever given satisfaction. Microscopic tests have been suggested, but these likewise fail to be of any practical value. Some observations made in our laboratory lead to the belief that if free lime is a real cause it is not the only one, as there is a physical side which must be taken into consideration.

Le Chatelier says that if one per cent of freshly calcined lime be added to a sound cement it will render it unsound. With this as a starting point, five well-known American brands of Portland cement, which passed the boiling test as received, were taken, and the above percentage of lime, freshly calcined over a blast lamp, immediately pulverised and added to the cement. None of them failed on the test. Larger quantities were then added, and with one brand 25 per cent of freshly calcined free lime was required before the cement failed on the

* Read at the Forty-fifth Annual Meeting of the A.C.S., at Washington. From the *Journal of Industrial and Engineering Chemistry*, iv., No. 5.

TABLE I.

No.	Brand and age.	Fineness (percentages).		Cement as received and CaO through 100-mesh (percentages).			Cement through 200 mesh and CaO through 100-mesh (percentages).		
		100-mesh.	200-mesh.	CaO (*a*).	H_2O (*b*).	Boiled.	CaO (*a*).	H_2O (*b*) (*d*).	Boiled.
1.	A. One month ..	95·2	82·4	5·0	27·0	O.K.			
				6·0	28·0	90			
1.	Two months ..			10·0	30·0	O.K.	12·0	34	O.K.
				12·5	33·0	95	15·0	35	95
				15·0	35·0	80	20·0	39	80
1.	Four months ..			12·5	33·0	O.K.	15·0	35	O.K.
				15·0	35·0	95	20·0	39	90
				17·5	36·0	90			
				20·0	38·0	80			
2.	A. One month ..	97·5	85·5	25·0	45·0	O.K.			
				(*c*)					
3.	B. One year.. ..	96·0	79·0	5·0	27·0	O.K.	8·0	30	90
				6·0	27·5	95	10·0	33	80
				7·0	28·0	90			
4.	C. One year.. ..	93·0	75·4	6·0	27·0	O.K.	8·0	30	90
				7·0	27·0	90	10·0	33	80
5.	D. One year.. ..	96·8	78·6	6·0	27·0	O.K.	8·0	31	90
				7·0	27·0	95	10·0	36	80
6.	E. One year.. ..			12·0	29·0	O.K.	12·0	29	O.K.
				15·0	30·0	95	15·0	31	95
							17·5	33	80

Analyses of Cements.

	1.	2.	3.	4.	5.	6.
Loss on ignition (*d*)	3·08	2·80	4·60	5·19	3·20	6·27
SiO_2	21·28	20·80	19·24	20·26	22·00	19·68
Fe_2O_3	9·02	9·50	10·52	9·32	9·00	11·00
CaO	62·24	62·40	60·98	60·09	62·30	58 60
MgO	2·68	2·75	2·78	3·34	2·64	3·18
SO_3	1·61	1·56	1·55	1·54	1·23	1·54

(*a*) Per cent of lime added.
(*b*) H_2O refers to the water used in making the pats.
(*c*) Greater amounts of lime made the pats too soft to be boiled after twenty-four hours.
(*d*) The high loss on ignition in several of these brands is due to the long seasoning in bags.

boiling test. The authority mentioned fails to say how finely the lime should be ground before adding to the cement, but it was presumed it should be at least as fine as the cement, hence it was quickly put through a 100-mesh sieve. The lime was obtained from a pure limestone at the highest temperature of a blast lamp. It might have been better to have used calcium nitrate as a starting point, but while these results are interesting, later tests showing the amount of water absorbed in passing from an unsound to a sound state shed a different light on the subject. The results of the tests are given in tabulated form.

In Table I. are also given the analyses and the fineness of the cements, to which reference will be made later. In one column are the results with lime sieved through a 100-mesh sieve and the cement as received, and in another column the cement after passing through a 200- and lime through a 100-mesh. It is necessary to explain that where "Boiled O. K." is used, it means the cement passed the test satisfactorily. To show degrees of soundness we use "Boiled 95 per cent" to mean checked slightly; "Boiled 90 per cent" to mean checked and softened slightly; "Boiled 85 per cent" to mean softened considerably; and "Boiled 80 per cent" to mean disintegrated entirely. These are only relative terms but they serve to indicate different degrees of soundness.

It will be noted in every case that the fineness of the cement played an important part, as when the particles coarser than 200-mesh were removed, the cement stood larger additions of lime. The inference is that the fineness of the cement, the fineness of the lime, and its degree of fusion play an important part. Unfortunately, brands B, C, D, and E were all over one year old when tested, but it will be noted that brand A, one month old, 85½ per cent passing a 200-mesh sieve, permitted 10 per cent greater addition of freshly calcined lime than the same brand two months old, 82·4 per cent fine and 2½ per cent more than the same per cent fine four months old, and that four coarser cements over a year old permitted the addition of less lime than the finer cement at two and four months.

Following this line and believing that the fineness of cement plays another part, a sample of cement 80 per cent passing a 200-mesh sieve, which failed badly on the boiling test, was ground in a mortar to 85 per cent fine and it showed improvement. In another portion ground 90 per cent fine, the improvement was more marked and in a portion ground 95 per cent fine the boiling test was perfect. We repeated this on various samples of cement with similar results. Thinking that possibly the free lime became hydrated from the moisture in the air while being ground, similar experiments were made by re-grinding in a laboratory tube mill with a rubber gasket, so that the negligible amount of moisture in less than ½ cu. ft. of air would have a negligible effect on hydrating the free lime in 15 lbs. of cement used in the test. Results were similar. Sieving to various degrees of fineness in a small room where it was presumed the atmosphere was fairly dry, owing to the presence of a number of trays of cement and lime on which experiments were being made, gave similar results.

Table II. gives the results of the average of five different samples of cement in each case, each treated in the following manner: grinding in a mortar, grinding in a tube mill and sieving. It will be noticed that the sample which was merely sieved to increase the fineness required a higher fineness as indicated by the 200-mesh sieve than the re-ground samples. This, of course, was to be expected :—

Table II.—*Effect of Fineness on the Boiling Test.*

	By re-grinding in mortar.	By re-grinding in tube mill.	Fineness regulated by sieving.
	Per cent.	Per cent.	Per cent.
81 per cent passing 200 mesh, as received ..	80	80	80
After bringing up to 85 per cent fine	85	85	80
After bringing up to 90 per cent fine	90	90	85
After bringing up to 95 per cent fine	O.K.	O.K.	90
After bringing up to 100 per cent fine	O.K.	O.K.	95

It might be argued that the free lime was largely in the particles removed by the sieve, but this is offset by the tube mill experiments which were of exactly the same cement except as to fineness, as nothing was added or removed, and if the failure when 80 per cent fine was due to free lime, the same free lime was present when it was 95 per cent fine, and if checking is due to free lime, this free lime in the 95 per cent fine was in a fine enough physical condition to become hydrated immediately on adding water when making the pat, or at least to become hydrated before the set had taken place. In the coarser samples it is possible that the free lime (if it is such) was present in the fused, glassy, coarser particles in such a way as to prevent its hydrating before the set had taken place, and the expansion took place on boiling the pat after it had hardened. The inference here is plainly that the degree of fineness is an important factor. The foregoing experiments apparently lead to the conclusion that a fair proportion of free lime is not injurious to a Portland cement if its physical condition is such as to permit it to be hydrated before the set has taken place. Hydrated lime is added to Portland cement with beneficial effect in some cases, and it matters not if the hydrated lime is added afterwards or free lime is in the cement when used, provided it is in a condition to be readily hydrated, assuming that all other conditions of balancing the chemical composition and manufacturing details are properly regulated.

It is often noted that a sample of cement which fails to pass the test one day may pass it very satisfactorily several days later, and it has frequently been noted where the change from very poor to very good took place in 24 hours. In some cases where the pats completely disintegrated on boiling, the cement became sound in three or four days, while with several brands samples have required thirty days or more to become thoroughly seasoned.

An effort was made to find what change took place in the ultimate chemical composition when a cement passed from an unsound condition to a sound one. If it is due to a hydration of the lime by atmospheric moisture, then the amount of moisture absorbed would be a gauge to the amount of free lime which had been hydrated, assuming (without any sound theoretical reason) that all the moisture taken up would go to hydrating lime, and none of it enter into the complex reactions which take place when larger amounts of water are used. A number of experiments were made by determining the loss on ignition on unsound cements and making the same test after the cement became sound. A more correct method would have been to absorb the water given off on ignition, as it is well known that cement absorbs carbon dioxide on seasoning and this also is given off on ignition, but a glance at the results will show the relatively small total difference that even if we assume it all to be water used in hydrating lime the amount of lime hydrated is comparatively small :—

Six tests showed a difference of 0·45 per cent in loss on ignition between the unsound and sound condition of the cement.
Six tests showed a difference of 0·75 per cent.
Six tests showed a difference of 0·90 per cent.

Realising the inaccuracy of the method, another set of experiments was conducted as follows :—The unsound cement was placed on cover glasses and carefully weighed. This was placed on a rack under a bell-jar. A tray of water was placed below it and the whole set on an iron plate over a Bunsen burner. The bottom was sealed by piling finely pulverised flint (100-mesh and finer) around the lip of the jar so that the air could not be renewed during the test. The temperature was raised to 150° F., and kept there from periods ranging from one to twenty-six hours. A very great number of these tests were made, and it was found that at 26 hours' heating, three samples of different cements absorbed 1·27 per cent, 1·84 per cent, and 2·02 per cent moisture. All of these, as expected, passed the boiling test perfectly.

Repeated trials were made to determine the minimum amount of absorption necessary to pass from an 85 per cent failing cement to a perfect test :—

Three tests showed 0·10 per cent was sufficient.
Five tests showed 0·19 per cent was sufficient.
Three tests showed 0·24 per cent was sufficient.
Three tests showed 0·27 per cent was sufficient.

Whether these are the minimum amounts is open to question, as a number of tests showed practically no absorption, yet it is apparent that moisture is essential to seasoning. Unsound samples kept in sealed jars a year still remained unsound, and samples heated to 150° F. in dry air remained unsound, yet the above shows that a trifling amount of moisture produced the desired result. Moisture is essential and heat accelerates the action, as to be expected. At lower temperatures it is necessary to absorb considerably more water to get results than at 150° F. Coarse cements required more water, and the problem becomes more complicated where the degree of burning of the clinker, the fineness of the raw material, and other manufacturing factors are taken into account.

Referring to the above tests where the minimum water was absorbed, it becomes apparent that in those cases, assuming all the moisture absorbed went to hydrating free lime, the maximum amount of free lime exerting the injurious influence could not have been over 0·31 per cent. Compare this with various amounts of free lime added, shown in Table I. It may be possible that the destructive expansion in the case of three cements requiring only 0·1 per cent water in seasoning was caused by the hydration of its equivalent of 0·31 per cent CaO, but it seems more probable that a physical explanation must also be considered in connection with it, for reasons briefly stated as follows :—

Lime calcined at highest heat of a blast lamp is not injurious to soundness when added in reasonable amounts to Portland cements. Lime calcined at the temperature attained in a rotary kiln does not become fused, hence when pulverised with the clinker should hydrate readily on the addition of water.

In burning of Portland cement clinker small particles of free lime may be encased in the fused mass of silicates, aluminates, &c. If subsequent grinding reduces this glass to a finely enough divided state, this lime will hydrate on addition of water and have no injurious effects. If free lime is the cause of disintegration, it seems that the state of fusion of the surrounding glassy clinker is directly responsible for it.

It is claimed that over-limed cements are most apt to fail on this test. It may be possible that owing to their being more difficultly fusible and requiring a higher temperature in the kiln, that a more glassy mixture envelopes the free lime. This furnishes room for microscopic study.

Under-burned cements may fail on this test. Free lime is given as the explanation of this.

If free limes is the real cause, then the fact that as little as one-tenth of 1 per cent of moisture will rectify many bad cases, leads to the belief that the phenomenon of seasoning is not so much one of hydrating free lime as it is a decrepitation process in which heat and moisture break up glassy particles, putting the lime in a physical condition to be hydrated, but not necesarily hydrating it. Acting on this idea, it was believed that cements become finer with age. A number of tests seemed to confirm this, but the breaking of the small per cent of coarser particles into finer ones takes place so slowly that differences of only 1 and 2 per cent were obtained in sieving, which may not be sufficient to offset the possible personal error in the sieving process. To get at the hydrating or decrepitation results, whichever it may be, only the residues left on a 200-mesh sieve were taken and sieved until no more would pass. These were exposed to air and moisture and again sieved each week. The following table shows the fineness of a sample of cement, part of which was exposed to air and part kept in a sealed jar for varying periods. Residues from the same cement were placed in an open jar and starting with nothing that passed a 200-mesh sieve, samples were sieved at various times, showing the per cent passing the 200-mesh after decrepitation had taken place.

TABLE III.—*Showing Fineness on a 200-Mesh Sieve.*

	Sample exposed to the air.	Sample kept in a sealed jar.	Sample of residues kept in an open jar.
	Per cent.	Per cent.	Per cent.
Starting point ..	84·6	84·6	0 0
After 14 days ..	85·0	85·0	5·0
After 33 days ..	85·8	85·0	5·6
After 49 days ..	86·0	85·4	6·0
After 91 days ..	86·0	85·4	7·6
After 107 days ..	86·2	85·6	7·6

As was to be expected, the sample kept in air increased in fineness more rapidly than the one in the sealed jar, and while sieving tests are subject to some variation and inaccuracies, these samples were tested on the same sieve by the same man and by the same method, hence the personal error is probably about the same in each case. The results of the samples exposed to air might be explained by the theory of hydration of free lime, but those on samples kept in a sealed jar must be explained by a physical theory of disintegration.

Summary.

While the work on this subject is by no means complete, it represents the results of some hundreds of tests, and at the present time points to the following as worthy of consideration :—

1. Only a thin film on the coarser particle of cement enters into the reactions on the setting of the same.

2. These coarser particles become finer with age.

3. The disintegration of these particles improves the soundness.

4. That if free lime is the cause of destructive expansion, three tenths of 1 per cent or less is sufficient to manifest itself.

5. That cases were noted where practically no absorption of water took place, hence cannot be explained by the hydration of free lime.

6. Cement kept in a sealed jar becomes finer with age, thereby indicating a mechanical decrepitation, which, as tests show, becomes more pronounced in the presence of moisture.

7. Carbon dioxide from the air, while it may aid in seasoning, is not essential, as shown by several series of tests.

8. That increasing the fineness of any particular sample of unsound cement improves its quality in this respect.

9. With the foregoing data, it appears that the theory of free lime as the sole cause of unsoundness is not well founded.

10. Expansion may be due principally to physical strains in the coarser particles.

11. Any theory of expansion on a purely physical basis seems inadequate, inasmuch as pats may frequently remain in boiling water several hours or more before destructive expansion becomes manifest. If it were merely the different rates of expansion, one would expect the rupture to take place shortly after the boiling begins.

12. With the data in hand at present, a possible theory presents itself as follows :—Seasoning of an unsound cement consists of decrepitation of the coarser particles, caused by or accelerated by heat and moisture, and that the moisture need not be in sufficient quantities to hydrate the free lime, but merely to render the coarser particles sufficiently fine to permit hydration before the set has taken place.

13. Le Chatelier claimed tri-calcium silicate to be the essential constituent of Portland cement and free lime as the agent destructive to soundness. Unger obtained *vitrified* tri-calcium silicate which disintegrated (seasoned), yet hardened well, while a *fused* tri-calcium silicate was unsound. This would indicate that if free lime is present in Portland cement, it is in the glassy unground particles.

14. O. Schott denied the existence of tricalcium silicates, tri-calcium aluminates, and tri-calcium ferrites in Portland cement, yet fused mixtures of these compositions showed the characteristic destructive phenomena found in unsound cements and which he attributed to free lime.

15. Michaelis claimed burning at too high temperatures produced unsound cements. Microscopic examinations of clinkers show a different physical structure of that from a rotary kiln and that burned at lower temperatures. The contradictory results obtained by investigators, both of synthetical mixtures and actual clinker, seem to be due to different degrees of fusion.

16. Shepherd and Rankin have demonstrated the existence of calcium tri-silicate, but the real cause of expansion is yet not conclusively proven.

17. What is needed now, in addition to the excellent work of the authorities herein mentioned and others unmentioned, is an investigation which will link together our knowledge on purely theoretical constitution of Portland cement clinker and the chemical and physical constitution of a commercial Portland cement, and further show what changes take place in passing from an unsound to a sound state.

Codeine in Commercial Morphine Sulphate.—J. B. Williams.—The author has found that specimens of morphine sulphate obtained in the United States contained from 0·9 to 7 per cent of codeine. Apparently when in the preparation of morphine sulphate the morphine is precipitated from a large volume of water, the codeine is partly carried down with the isomorphic morphine crystals.—*American Journal of Pharmacy*, lxxxiv., 391.

Preservation of Samples of Milk.—G. Denigés.—Although potassium bichromate is in some circumstances a useful antiseptic for the preservation of milk, a more valuable reagent is an alcoholic solution of phenol made by dissolving 50 grms. in 10 cc. of alcohol. The author analysed in 1900 a sample to which phenol had been added, and repeated the analysis in 1910, obtaining remarkably concordant results which testify to the value of the antiseptic.—*Annales des Falsifications*, No. 50, p. 559.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, February 27th, 1913.

Sir Archibald Geikie, K.C.B., President, in the Chair.

Mr. F. Soddy, F.R.S., made an oral communication to the Society upon the Periodic Law from the standpoint of Recent Results in Radio-activity.

Papers were read as follows :—

"*Thermal Properties of Carbonic Acid at Low Temperatures.*" By C. F. Jenkin and D. R. Pye.

The paper describes a series of experiments made in the Engineering Laboratory at Oxford undertaken with the object of checking by direct measurements the accuracy of the accepted CO_2 Entropy-temperature diagram, due to Mollier, and of extending the diagram to lower temperatures, *i.e.*, from $-30°$ C. to $50°$ C.

Mollier's diagram was calculated mathematically from an assumed characteristic equation, an empirical equation to the pressure-temperature curve, and Amagat's data on Liquid and Vapour Densities. Our diagram is plotted directly from measurements of the quantities of heat represented on the diagram, a method which has not been used before.

The heat measurements were made in two electrically-heated calorimeters which formed part of a CO_2 vapour compression freezing machine; by using two calorimeters the heat given to the CO_2 in any selected part of the cycle could be isolated from the rest, and measured. Special arrangements were devised for weighing the CO_2, so that the rate of flow could be accurately determined. All the tests were made when the apparatus had reached a steady state and was working at a uniform rate under constant conditions.

The experiments include the direct measurement of the following quantities:—

The total heat of the liquid.
The latent heat of the liquid.
The Joule-Thomson effect for the liquid.
The dilatation and elasticity of the liquid.
The specific heat of the gas.

Most of these measurements are new. With these results a $\theta\phi$ diagram has been constructed (including constant I lines) from $+20°$ C. to $-50°$ C. This diagram differs slightly from Mollier's and is believed to be more accurate. Accurate data are of considerable importance, not only to physicists but also to engineers, owing to the extensive use of CO_2 freezing machines on board ship for cold storage, &c.

"*Re-reductions of Dover Tidal Observations, 1883—1884, &c.*" By Edward Roberts.

"*Formation of Anthocyan Pigments in Plants.* Part IV. *The Chromogens.*" By Prof. F. Keeble, E. F. Armstrong, D.Sc., and W. N. Jones.

The results of the experiments described in this paper lend support to the hypothesis that the anthocyan pigments of plants are produced by the oxidation of colourless chromogens.

Under certain conditions a coloured flower may be caused to reverse its pigment-forming process and to reduce the pigment which it contains to a colourless state. By again changing the conditions the pigment-forming mechanism may be made to resume activity and to give rise to pigments identical in colour with those of the normal intact flower. Whether the flower forms pigment or remains colourless depends on the degree of hydration of its tissues. If water be withdrawn from the tissues oxydase activity falls off, the activity of "reducing-bodies" becomes increased—actually or relatively—pigment formation is inhibited, and the pigment in existence already is reduced to chromogen. The flower becomes colourless. If water be supplied to the decolorised tissues, oxydase resumes its activity and chromogens are oxidised to pigments.

The most efficient agent for bringing about decoloration is strong alcohol. Thus red, pink, purple, and white-flaked purple flowers of Brompton stocks become decolorised when immersed in 98—99 per cent of alcohol. In water the petals recover their original colours with rapidity. If the re-formed pigment be allowed to diffuse away a further supply may be induced to form by treating the petals with hot water. It follows that the chromogen reserves of the plant are in large excess of the amounts required for normal pigment-formation.

The reducing body which inhibits and reverses the pigment forming process in the petals of flowers exercises a like action on other similar oxidation processes. Thus when added to a brass peroxydase, shown previously to be capable of oxidising benzidine, it inhibits this action, and, moreover, if added to the product of the action of oxydase on benzidine, the characteristic blue colour of that product is discharged.

The benzidine reagent is therefore of great value in biochemical investigations, serving not only as an indicator of plant-oxydases, but also for detecting the presence of reducing bodies.

The decisive part which the degree of hydration plays in determining whether oxidation or reduction processes shall predominate in vegetable tissues appears to have an important bearing on such phenomena as the latency and activity of seeds and the awakening of plants from winter rest.

"*Formation of the Anthocyan Pigments of Plants.* Part V. *The Chromogens of White Flowers.*" By W. N. Jones.

The paper, which deals with the biochemistry of the pigment forming mechanism contained in white flowers, is a continuation of the work summarised in Part IV. of the present series of communications. As shown in the latter paper, the pigments of flowers may be reduced to the state of colourless chromogens and may be re-formed by artificial means from those chromogens.

In the present paper it is shown that chromogens may be obtained from some white flowers and may be caused by similar treatment to give rise to pigments. That the chromogens of such white flowers are those which in coloured forms are responsible for the anthocyan pigments, is indicated by the facts that their distribution coincides with the distribution of pigment in coloured varieties of the several flowers, and that the treatment which causes the production of pigment in white flowers results in the formation of additional pigment in some coloured flowers.

An investigation of the white flowers of several plants demonstrates that whereas in some species lack of colour is to be ascribed to lack of chromogen, in others it is due to the failure of chromogen and oxydase to interact with one another though both are present in the flowers. In these latter cases it may perhaps be inferred that oxydase and chromogen are located in different parts of the tissues.

The chromogens extracted from white flowers may be used in place of artificial chromogens, such as benzidine, &c., to determine the localisation of oxydase in flowers of the same or other species of plants.

"*Changes in the Breathing and the Blood at Various High Altitudes.*" By Mabel P. FitzGerald.

The observations described in the paper were made during the summer of 1911 on persons residing in towns, mining camps, &c., at various altitudes from 5000 to 14,000 feet in the Colorado portion of the Rocky Mountains. The investigation was undertaken in connection with the Pike's Peak Expedition, the results of which have already been communicated to the Royal Society by Messrs. Douglas, Haldane, Yandell Henderson, and Schneider.

The main conclusions reached are as follows:—

1. The volume of air breathed per unit mass of CO_2 produced by the body is always increased in persons acclimatised at high altitudes. The mean increase of breathing is such as to produce a fall of about 4·2 mm. (or roughly 10 per cent of the normal for sea-level) in the partial pressure of CO_2 in the air normally present in the lung alveoli for every 100 mm. of fall in the barometric pressure. Both men and women show this fall, after allowance is made for the normal difference in the alveolar CO_2 pressure of men and women.

2. The percentage of hæmoglobin in the blood of acclimatised persons is likewise increased, the mean increase being about 10 per cent of the normal at sea-level in men for every 100 mm. of diminution in the barometric pressure. Both men and women show this fall.

3. It may take some weeks for these changes to establish themselves fully in persons passing to a high altitude or to disappear in persons passing to sea-level.

Charts are given, showing the results graphically, together with the relations between altitude and atmospheric pressure, and the relations between barometric pressure and the *percentages*, as well as the partial pressures, of the CO_2 and O_2 in the alveolar air.

The increased breathing and percentage of hæmoglobin are evident adaptations to the shortage of oxygen consequent on the diminished atmospheric pressure.

CHEMICAL SOCIETY.

Ordinary Meeting February 20th, 1913.

Prof. PERCY F. FRANKLAND, LL.D., F.R.S., President, in the Chair.

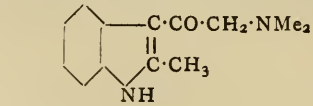
(Concluded from p. 117).

45. "*Absorption Spectra of Substances containing Labile Hydrogen Atoms.*" By PETER JOSEPH BRANNIGAN, ALEXANDER KILLEN MACBETH, and ALFRED WALTER STEWART.

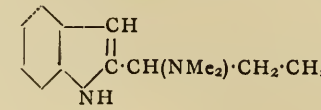
An examination of various compounds containing a displaceable hydrogen atom showed that they may be divided into two classes:—(*a*) Those which, whilst showing only general absorption in alcoholic solution give rise to a banded absorption in presence of alkali; and (*b*) those which do not conform to this rule, even when the sodium derivative can be isolated. With regard to the first class of compounds it has been found that several derivatives of malonic acid develop bands the penetration of which is dependent on the amount of alkali present in the solution. This confirms Hantzsch's observations on ethyl acetoacetate. The bands are evidently due to the presence of the sodium derivatives of the various substances, and have nothing to do with the tautomeric changes assumed by Baly and Desch to explain their existence. To explain the difference between the spectra of the enolic form and the sodium salt, Hantzsch's suggestion of internal complex salt formation may be accepted, or an alternative one based on Gebhard's views on affinity may be employed. In either case it seems that if a band is to be produced by the sodium salt the sodium atom must come into the 1 : 5- or 1 : 6-position with regard to a carbonyl group, as the sodium derivative of urethane shows no band in its spectrum. A similar explanation can be put forward to account for the presence of the band in the spectrum of ethyl β-aminocrotonate.

46. "*Researches on the Constitution of Physostigmine.* Part II. *The Synthesis of* 3-*Dimethylaminoacetyl*-2 *methylindole and* 2-α-*Dimethylamino* γ-*hydroxypropylindole.*" By ARTHUR HENRY SALWAY.

The author described the synthesis of two indole derivatives containing an aliphatic side-chain, which is oxygenated, and possesses a tertiary basic nitrogen atom, in combination with the indole nucleus, namely:—



and –



These substances were prepared for the purpose of comparing their properties with those of eseroline, $C_{13}H_{18}ON_2$, which has previously been shown (*Trans.*, 1912, ci., 988) to contain, in all probability, an indole complex.

As a result of the investigation it is concluded that eseroline is not a simple indole compound containing an open side-chain.

47. "*Contributions to our Knowledge of Semicarbazones.* Part II. *The Semicarbazones of Mesityl Oxide.*" By FORSYTH JAMES WILSON and ISIDOR MORRIS HEILBRON.

A semicarbazone of mesityl oxide (α semicarbazone) melting at 164° has been prepared by Scholtz (*Ber.*, 1896, xxix., 612), and further investigated by Harries and Kaiser (*Ber.*, 1899, xxxii., 1338). The authors find that this α-semicarbazone when exposed in chloroform solution to ultra-violet light is partly converted into a stereoisomeride (β-form) melting at 133—134°, the difference between the two forms being due to nitrogen isomerism in the sense of the Hantzsch-Werner hypothesis. The differences between the four semicarbazones of phenyl styryl ketone previously studied by the authors (*Trans.*, 1912, ci., 1482) is due to nitrogen stereoisomerism, combined with carbon stereoisomerism, whilst in the present case carbon stereoisomerism is excluded. The two modifications give practically identical absorption spectra, which are not affected by alkali; also, they undergo no change of colour in light. In order that absorption may be affected by alkali and phototropy be evident, the authors conclude that carbon and nitrogen stereoisomerism are both necessary.

The α-semicarbazone on distillation yielded a substance melting at 129°, which is probably cyclic in structure (Scholtz, Harries, and Kaiser, *loc. cit.*). The same compound can be obtained by distilling the β-semicarbazone, a transformation of the β- into the α-form first taking place.

On exposure in chloroform solution to ultra-violet light both modifications are partly converted into one another, an equilibrium between the two forms being established.

48. "*Oxidation of the Nitro-o xylenes with Dilute Nitric Acid.*" By CHARLES HORNE WARNER.

The two mononitro-*o*-xylenes are readily oxidised with dilute nitric acid, giving in almost quantitative amount the corresponding nitrophthalic acids (*Trans.*, 1909, xcv., 207). In view of this fact it seemed of interest to investigate the behaviour of this reagent towards the di- and tri-nitro-*o*-xylenes, especially since some of the nitrophthalic acids which it was hoped to obtain were required for comparison with substances resulting from other reactions. The oxidations do not, however, proceed smoothly; the nitrophthalic acids are only obtained in small amounts, and the products are not easily isolated in a pure condition.

When 3 : 5-dinitro-*o*-xylene (*Ibid.*, p. 209) was oxidised with dilute nitric acid in sealed tubes, it yielded a liquid and a solid product. On evaporation, the former gave 3 : 5-dinitro-*o*-phthalic acid (compare Merz and Weith, *Ber.*, 1882, xv., 2708), which could not be completely purified by crystallisation alone, but was obtained, melting at 225°, through its monoethyl ester (Beilstein and Kurbatov, *Annalen*, 1880, ccii., 227). The acid crystallises from water saturated with hydrogen chloride in long, thin, flattened needles. The *diethyl* ester, obtained by heating the silver salt in a dry benzene solution of ethyl

iodide, separates from alcohol in fine colourless needles, melting at 73°. The *anhydride* was prepared by heating the acid with excess of acetyl chloride. It crystallises from a mixture of ethyl acetate and light petroleum (b. p. 40—60°) in stout colourless needles, melting at 161°. Water very readily re-converts it into the acid, exposure to laboratory air being sufficient to effect this change.

From the solid product mentioned above there was isolated 3 : 5-dinitro-*o*-toluic acid melting at 206° (compare Jacobsen and Wierss, *Ber.*, 1883, xvi., 1959).

3 : 4-*Dinitro-o-phthalic acid* was obtained by the oxidation of the corresponding dinitro-*o*-xylene with dilute nitric acid. It separates from concentrated hydrochloric acid in small colourless needles, melting and evolving gas at 204—205°. The *diethyl* ester, prepared through the silver salt, crystallises from alcohol in colourless needles melting at 69°.

3 : 4-*Dinitro*-o *toluic acid*, which is produced in the above reaction, crystallises from a mixture of ethyl acetate and light petroleum (b. p. 40—60°) in stout colourless needles, melting at 182°. The *diethyl* ester was prepared from the silver salt of the acid ; it separates from alcohol in colourless rectangular plates, melting at 63°.

Both 3 : 4 : 5-trinitro- and 3 : 4 : 6-trinitro-*o*-xylene appear to be completely decomposed when heated with dilute nitric acid in sealed tubes.

49. "*Phosphonium and Ammonium Iodides.*" By ALFRED HOLT and JAMES ECKERSLEY MYERS.

Phosphonium iodide vapour decomposes on heating when it is dry, rendering the purification of this substance by sublimation extremely difficult.

The substance appears to be unchanged when sublimed in the presence of traces of water vapour.

The behaviour of ammonium iodide under similar conditions was described as a comparison.

50. "*Phosphoric Acids and some Phosphates.*" By ALFRED HOLT and JAMES ECKERSLEY MYERS.

Experiments with two polymeric forms of metaphosphoric acid were described, and it was shown that the hydration of the mono-variety is unimolecular.

Experiments with glacial phosphoric acid lead to the belief that its vapour does not have a composition corresponding with the formula HPO_3.

Examination of the metaphosphates of the alkalis failed to give evidence that they are derived from acids other than mono- and tri-metaphosphoric acids.

51. "*Optical Activity and Enantiomorphism of Molecular and Crystal Structure.*" By THOMAS VIPOND BARKER and JAMES ERNEST MARSH.

It was pointed out that no molecular configuration is enantiomorphous unless it is devoid of all the following three elements of symmetry—plane, centre, and alternating axis. Enantiomorphism is, however, compatible with the presence of ordinary axes of symmetry, so that an enantiomorphous structure is not necessarily asymmetric, that is, totally devoid of symmetry.

The discussion of the conditions necessary for optical activity in the liquid and crystalline states leads to the conclusion that the optical activity of crystals of magnesium sulphate, monohydrated sodium dihydrogen phosphate, Schlippe's salt, sodium uranyl acetate, sodium chlorate, and sodium bromate cannot be referred to a spiral arrangement of the molecules in the crystal edifice, which arrangement is possible in quartz, cinnabar, and others, but must be due to the same cause as the optical activity in crystals of sucrose, namely, an enantiomorphous configuration of the molecule. Enantiomorphous constitutions developed on lines of co-ordination were proposed for the six substances in question. The inactive character of the solutions was attributed to auto-racemisation.

52. "*Some Double Salts with Acetone of Crystallisation and the Crystallisation of Silver Iodide, Silver Bromide, and Cuprous Iodide.*" By JAMES ERNEST MARSH and W. C. RHYMES.

The iodides of silver, lead, and copper form double salts with the alkali metal iodides, which are readily soluble in acetone. Many of these salts crystallise well on evaporation of the acetone in dry air. The rubidium silver salt has the composition $RbI,2AgI,2C_3H_6O$, the potassium salt $KI,2AgI,2C_3H_6O$, and the ammonium salt, which crystallises in a different form, $NH_4I,2AgI,3C_3H_6O$. These salts lose acetone readily on exposure to air. The potassium salt slowly deliquesces, and ultimately crystals of silver iodide are deposited from the solution thus formed.

If lithium iodide and silver iodide in the proportion of LiI to 2AgI are dissolved in acetone and the solution is exposed to the air, no double salt separates, but large transparent crystals of silver iodide gradually form. Silver bromide has been obtained well crystallised from solution in lithium bromide and acetone. Crystalline cuprous iodide has also been obtained from solution in lithium iodide and acetone.

53. "*Relation between the Absorption Spectra of Acids and their Salts.*" By ROBERT WRIGHT.

An examination of the absorption spectra in aqueous solutions of a number of acids and their sodium salts seems to justify the following conclusions :—(1) There is not of necessity a relation between absorptive power and degree of ionisation, for many feeble acids show the same spectra as their highly ionised salts. (2) Although change of absorptive power on salt formation may in some cases be due to a difference in the structures of the acid and its salt, still many acids show spectra different from those of their salts, even when such change of structure in the molecule is hardly possible.

54. "*Synthetical Experiments in the Group of the* iso*-Quinoline Alkaloids.*" Part III. *The Constitution of Anhydrocotarnineacetophenone, &c., together with an Account of some New Condensation Products of Cotarnine.*" By EDWARD HOPE and ROBERT ROBINSON.

The authors have submitted to a careful examination the condensation products of cotarnine with acetophenone and ethyl phenylacetate, which were first described by Liebermann and his co-workers (*Ber.*, 1904, xxxvii., 211), and regarded by them as derivatives of N methylaminoethylbenzaldehyde. It is now found that these substances are in reality derivatives of tetrahydro*iso*quinoline, and are therefore constituted analogously to narcotine and hydrastine. New condensation products of a similar nature have been prepared by the condensation of cotarnine with phenylacetonitrile, 1-hydrindone, 1 : 3-diketohydrindene, indene, isatin, fluorene, and 1-methylindole.

55. "*Identification of Ipuranol and some Allied Compounds as Phytosterol Glucosides.*" By FREDERICK BELDING POWER and ARTHUR HENRY SALWAY.

It has previously been recorded in connection with the description of ipuranol and some allied compounds to which distinctive names and formulæ had been assigned, such as citrullol, trifolianol, ipurganol, bryonol, cluytianol, &c., that they yield colour reactions very similar to those given by the phytosterols. The observation has now been made that several of these compounds, when heated under suitable conditions with aqueous hydrogen chloride, undergo hydrolysis, with the formation of a phytosterol and dextrose. The formula originally assigned to ipuranol, namely, $C_{23}H_{40}O_4$, requires C = 72·6 ; H = 10·5, whereas a sitosterol glucoside, $C_{33}H_{56}O_6$, requires C = 72·3 ; H = 10·2 per cent, and the latter figures are likewise in excellent agreement with the analytical results recorded for ipuranol and some allied compounds. The hydrolysis of ipuranol may therefore be represented by the following equation : $C_{33}H_{56}O_6 + H_2O = C_{27}H_{46}O + C_6H_{12}O_6$.

It is concluded that all the compounds of the type of ipuranol are glucosidic in character, although the phytosterols obtained by their hydrolysis are not in all cases identical. In place of the distinctive names which have previously been assigned to a number of these substances, it is proposed to designate them collectively as *phytosterolins*.

PHYSICAL SOCIETY.

Ordinary Meeting, February 28th, 1913.

Prof. A. SCHUSTER, F.R.S., President, in the Chair.

A PAPER on the "*Interference of Röntgen Radiation*," by Prof. C. G. BARKLA and Mr. G. H. MARTYN, was read by Prof. BARKLA.

The authors have made a preliminary investigation of the Röntgen radiation proceeding from a crystal of rock salt (which is of the simple cubical form) when a pencil of Röntgen radiation is incident in a direction nearly grazing one of the three sets of mutually perpendicular cleavage planes.

Reflection of X-rays by the Cleavage Planes.—Using a very narrow pencil of radiation, it was seen that the principal secondary pencil was one obeying the laws of reflection from the cleavage planes.

A pencil diverging in all directions from a point source produced a corresponding reflected pencil of radiation converging to a line focus after reflection from a set of parallel cleavage planes. The quality of the radiation forming the secondary pencils was shown both by the photographic and by the ionisation method to be, not the fluorescent X radiation, but of the kind previously described as scattered X-radiation. It was approximately of the same penetrating power as the primary radiation, and was approximately homogeneous, having traversed 5 mm. of rock salt in the case investigated.

Interference Fringe Systems.—A diverging pencil of radiation was directed on to a crystal so that various portions were incident on the cleavage planes at different angles. A photographic plate showed the relative intensity of the corresponding reflected radiations. It was seen that the intensity of the reflected pencil varied periodically with varying angle of incidence, the maximum being separated by intervals corresponding to approximately equal increments in the value of $\cos\theta$, where θ was the angle of incidence on the reflecting planes.

Such a series of maxima may be explained by interference of the pencils reflected from equal spaced parallel planes, the maxima being spectra of various orders.

The wave-length, calculated on the assumption that these are planes passing through corresponding portions of molecules in the planes of cleavage, and that a molecule is simply NaCl, is found to be $0{\cdot}6 + 10^{-9}$ cm. If the molecule be more complex, the calculated wave-length would be greater. This value thus agrees remarkably well with the value (between 1 and 2×10^{-9} cm.) calculated from the velocity of ejection of electrons by this X-radiation, taking this to behave as ultra-violet light of short wave-length.

Using a more extended source the above "spectral lines" became indistinct and disappeared, but there appeared a periodic variation in intensity, the band-width being about four times the distance between the above lines. Such a system of interference bands would be produced by a second plane of reflection within the molecules in a position dividing the distance between the other planes in the ratio 1 : 3 approximately. All the evidence considered indicates that these effects are due to interference. Various crystals were used, and one was turned through a right angle so that another system of planes acted as reflecting planes.

The only experiment made up to the time of writing on the effect of varying the penetrating power showed a 25 per cent smaller band-width with a radiation of increased penetrating power. Further experiments are, however, being made.

Finally, there can be little doubt that the fringe systems are interference fringe systems. That the smaller system is a series of spectra of different orders and the other an interference band system seems probable; this theory certainly explains the results observed up to the time of writing.

The PRESIDENT remarked that Prof. Barkla, in explaining the second system of fringes, assumed that each molecule contained an excentrically placed electron similarly situated, and that all these electrons were stationary, which was contrary to the usual ideas on the subject. Prof. Barkla also rather sharply distinguished between regular reflection and scattering. But regular reflection could be considered to be due to a system of scattered wavelets.

Prof. C. H. LEES thought it was surprising to see that the results were capable of such a simple explanation, and hoped that such experiments would lead to more knowledge of the structure of the molecules.

Prof. J. W. NICHOLSON pointed out that if the molecule had been assumed to be more complex than NaCl the wave-length obtained would have been greater.

Dr. G. W. C. KAYE remarked that these experiments constituted a fresh blow to the corpuscular theory of the X-rays. The present experiments showed a great similarity between X-rays and ordinary light. Had Prof. Barkla used other crystalline substances? He hoped that the results obtained with rock salt could be generalised from.

Mr. C. E. S. PHILLIPS inquired about the time of exposure necessary. Had Prof. Barkla made experiments with mica or star-mica? Some experiments with these substances made at the Cancer Research Hospital showed irregularities they could not easily explain.

Mr. D. OWEN remarked that the experimental results were interpreted by the author as implying the existence of homogeneous etheric waves. It seemed, however, unthinkable that radiation of definite wave-length could be emitted from the anti-cathode of the X-ray bulb, considering that the exciting cause of the production of these rays was the bombardment of the metal by cathode-ray particles. The values deduced for the wave-length were of the same order as the dimensions of the molecule. This result suggested that the definiteness of structure of the rays was imparted by the arrangement of the molecules in the crystals employed, that this definiteness existed only *after* the crystal had produced its effect, and that what was being measured was not the wave-lengths of the incident radiation but the distance apart of the molecules. Might not the phenomena be then of the same kind as those occurring in the "palisade effect" in acoustics? It would be of interest to know whether the wave-lengths found depended on the nature of the X-ray bulb, whether "hard" or "soft."

Prof. BARKLA, in reply, stated that according to chemists the molecule of rock salt might be Na_8Cl_8, which would make the wave-length twice as great. When the full anti-cathode was used the exposure given was four or five hours. With a restricted pencil the exposures given sometimes amounted to eighteen hours. The crystal plates employed were 2 mm. to 5 mm. thick. After passing through this plate the rays were very homogeneous. One of the things that the corpuscular theory of X-rays had been put forward to explain was the fact that the X ray seemed to possess all the energy of the electron which gave rise to it. But the same was true in the converse case of the emission of electrons caused by ultra-violet light. Some recent experiments had been made with polarised X rays. The rays were absorbed by a carbon block, and the polarised scattered radiation emitted at right angles was employed. When these rays were allowed to impinge obliquely on metal surfaces the effect depended upon the orientation of the plane of polarisation in a way easily explained by the pulse theory, but inexplicable on the other.

The PRESIDENT raised a question as to what was meant by the homogeneity of the X-rays. Did it mean that the wave-lengths comprised might be limited to, say, an octave or less?

Prof. BARKLA replied that after the rays had passed through the plate of rock salt no heterogeneity whatever could be detected in them. Each additional plate produced just the same effect. They were probably as homo-

geneous as some spectrum lines, say, the light from a sodium flame.

The PRESIDENT remarked that this only showed that the coefficients of absorption of the different wave-lengths were equal.

Prof. BARKLA replied that the coefficient of absorption did vary with the wave-length.

The PRESIDENT stated that if any such homogeneity existed in X-rays it did away with the pulse theory of their origin.

Mr. A. EAGLE (communicated remarks) considered that ordinary X-rays consisted of a random succession of random sized pulses, while homogeneous X-rays consisted of a random succession of more or less equal and similar pulses. The only conclusion that could be drawn, from the fact that passing through an additional thickness of an absorbing medium produced no qualitative change in the rays, was that the pulses were capable of travelling through the medium without appreciable change of form (save perhaps that due to a diminished amplitude). To imagine that these experiments showed that X-rays contained periodic wave trains consisting of many thousand oscillations similar to spectrum lines, was, he considered, quite unjustifiable. Any evidence of definite wave-lengths found in the rays after passing through a crystalline plate was manufactured by the regular periodicity in the spacing of its molecules, exactly as homogeneous light is manufactured by a grating out of the pulses of white light. But this is by no means saying that the wave lengths obtained will depend upon the particular nature of the crystal used.

A paper on "*Alternating-current Magnets*" was read by Prof. E. WILSON.

It follows from the well-known law of pull of an electromagnet that if the magnetic field alternates between positive and negative values the pull is unidirectional and intermittent. Unless means are provided to reduce the consequent chattering and vibration, the magnet is rendered useless. In the present experiments a phase-splitting device has been adopted, and consists in surrounding a portion of the pole-piece of the magnet with a short-circuited coil. The portion of the pole-piece so surrounded is sometimes said to be "shaded," and the coil referred to as a "shading" coil. The effect of this coil is to alter, not only the relative amplitudes, but the phase of the magnetic fields passing through the shaded and unshaded portions of the pole face. The magnet used in the experiments varies the length of its gap when in action, and the influence of the gap length upon this phase-displacement has been studied. When the resistance of the shading coil is such that the magnetic induction B over the whole face is substantially uniform and the gap closed, the phase displacement was 72 electrical degrees (360 deg. = 1 period). A gap length of 0·15 cm. reduces the phase displacement to 18° and consequently the minimum or "hold on" pull drops. This minimum or "hold on" pull is, of course, smaller than the average, and has to be taken into consideration in the design of the magnet. The arrangement of the shading coil above described is very effective in preventing vibration and chattering when the magnet is closed, and renders the alternating-current magnet a practical success.

With constant alternating voltage impressed upon the magnetising coils of the magnet the net pull exerted diminishes rapidly at first as the gap length increases and tends to become more nearly constant. The R.M.S. ampères, on the other hand, steadily increase as the pull diminishes owing to the increase in the gap length.

The observed net pull in the case of the magnet experimented upon is less than the calculated average pull, varying from 83 to 59 per cent as the gap length varies from 0 to 1 cm.

Mr. T. HARDING CHURTON asked at what frequencies the result had been obtained, as the chattering would, of course, be greatest at low frequencies. He was surprised to see that such a large displacement as 72° could be obtained due to shading.

Prof. E. WILSON, in reply, stated that the frequency used was 50. The large displacement of phase only occurred when the air-gap was small, but it was only when the armature was actually in contact with the pole that it was required to abolish the chattering.

SOCIETY OF CHEMICAL INDUSTRY.

(LONDON SECTION).

Ordinary Meeting, March 3rd, 1913.

Dr. W. R. HODGKINSON in the Chair.

THE following papers were read and discussed:—

"*Notes on Chinese Antimony Ores and Regulus.*" By W. R. SCHOELLER.

Crude antimony is obtained from high grade ores in the province of Hu-nan by liquation. The Chinese estimate the value of ores by passing 100 lbs. through the actual process, and describe the ores according to the amount of crude obtained. These ores usually run about 58 per cent of antimony.

The author frequently noticed in the assay of crude antimony that the antimony slightly exceeded in amount that required by the formula Sb_2S_3. (The sulphur was found to be several per cent below the figure demanded by the formula Sb_2S_3). This result was attained by determination of the sulphur by three different methods. The author suggests that the presence of oxide accounts for this deficiency of sulphur, and describes experiments intended to investigate this point. The liquated sulphide of antimony, unlike stibnite, is strongly attacked by bitartrate solution.

"*Notes on Thermometry.*" By J. H. COSTE.

The author refers to the following errors to which mercury in glass thermometers is liable. Those peculiar to the combination of mercury and glass, (1) deviation of scale from hydrogen scale; (2) temporary depression of zero after heating. These errors, to a certain extent, compensate one another between 0° and 100°. The composition of various glasses used in modern thermometry is given. Errors proper to each individual thermometer are:—(3) Incorrect value or position of the fundamental interval; (4) inequality of bore of capillary. Other errors partly dependent on the glass used and partly on the construction of the instrument are:—(5) Dilation of the bulb caused by the internal pressure of the mercury column; (6) external pressure on bulb. Errors dependent on method of using are:—(7) Stem correction; and (8) lag.

The precautions necessary for obtaining various orders of accuracy are indicated, and the use of carefully examined thermometers is advocated. The use for many purposes of short thermometers is recommended as reducing the serious error in corrections for exposed columns at high temperatures.

The use of thermoelectric thermometers for temperatures above 300° is advised.

"*Heat Test on Guncotton, Nitroglycerin, and Cordite.*" By A. EGERTON.

The author discusses the real meaning of the heat test as usually applied, alluding at some length to the work of Robertson and Smart, and describes a great deal of experimental work undertaken with a view to further investigating the test as usually applied.

He also describes a new form of test in which the use of paper is avoided. The reagent used is a mixture of solutions of α-naphthylamine and sulphanalic acid or a solution of dimethyl aniline.

The theoretical bearings of the test in its various forms are very fully discussed.

NOTICES OF BOOKS.

Digitalis Assay. By W. HARRISON MARTINDALE, Ph.D. (Marburg), F.C.S. London: H. K. Lewis. 1913.

THIS book contains a communication made to the Pharmaceutical Society at a recent meeting in London, in which the author described a simple colorimetric method of testing digitalis tincture. Brief abstracts were first given of chemical methods which have been proposed for assaying, and also of the physiological method of standardising, and then the details of the author's method were described, and the results obtained by it carefully compared with those deduced from physiological experiments. The scale of colours employed is reproduced, and the author claims that it is quite easy to determine by a simple and rapid chemical process whether a given tincture is above or below standard. Some notes are added on the conditions of growth of digitalis and the conclusions which have been drawn as to the potency of leaves gathered in given circumstances.

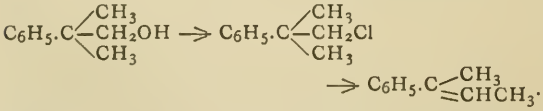
General Chemistry of the Enzymes. By HANS EULER. Translated by THOMAS H. POPE. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1912.

THE author of this book, believing that the time had come to study the general results which may be deduced from the investigation of the chemistry of the enzymes and the accumulated data concerning them, endeavoured two years ago to harmonise the facts with the theories of physical chemistry. Of the book then published in German this is a translation, with some additions and alterations. Some sections, for example those on the glucosides and the fermentation enzymes, have been entirely re-written. The physical properties of enzymes and the chemical dynamics of enzyme reactions are summarised, and as far as possible all known experimental data in connection with enzyme reactions are carefully enumerated. The author gives short accounts of the practical methods which have been employed in investigations, and throughout his *résumé* shows strict impartiality and a due sense of proportion.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Heddomadaires des Séances de l'Académie des Sciences. Vol. clv., No. 27, December 30, 1912.

Formation of Dimethylstyrolene from Phenyldimethylethyl Alcohol.—A. Haller and Edouard Bauer.—When phenyldimethylacetamide is reduced by means of sodium and absolute alcohol, primary phenyldimethylethyl alcohol is obtained as well as 2-phenyl-2-methyl-1-propylamine, previously prepared by Wallach by reducing phenyldimethylacetonitrile. This new alcohol, when subjected to the action of thionyl chloride, gives a chloride of unknown constitution, and the unsaturated hydrocarbon 2-phenyl-2 butene or dimethylstyrolene :—



Relation between Conductivity of Acids and their Absorption by Skins.—André Brochet.—The absorption of acids by skins is a general phenomenon, and results from a chemical combination, for whatever the acid employed the quantity absorbed is proportional to the chemical equivalent. This quantity, while remaining of the same order of magnitude, is rather smaller in the case of feebly dissociated acids.

Bulletin de la Société Chimique de France. Vol. xiii.—xiv., No. 1, 1913.

Rate of Decomposition of Hydrogen Peroxide by Heat.—Georges Lemoine.—The irreversible decomposition of hydrogen peroxide under the influence of heat is regulated by the proportion of water existing at each instant in the liquid, and thus water acts as a catalyst. This result explains the extreme slowness of the decomposition of concentrated hydrogen peroxide.

Electrolysis of Cyclopentanone.—Marcel Godcho and Felix Taboury.—When cyclopentanone is electrolysed some α-cyclopentylidene cyclopentanone is formed. In the fraction which passes over on distillation under 25 mm. between 230° and 255° a compound of formula $C_{20}H_{28}O$ is found, and $C_{20}H_{30}O_2$ is present in the residue of the distillation *in vacuo*. The former is a dicyclopentylidene derivative of Meiser's pinacoline, while $C_{20}H_{30}O_2$ is the corresponding pinacone.

Determination of Iron in Water.—E. Tassilly.—It is possible to determine the amount of iron in waters by observing the coloration given by ferric chloride in presence of sulphocyanide, if a spectrophotometer is used as a measuring instrument. Twenty cc. of hydrochloric acid are boiled with 100 cc. of water. Then 0·5 to 1 grm. of potassium chlorate is added, and heating is continued until chlorine begins to be evolved. The liquid is then cooled, 20 cc. of sulphocyanide solution containing 17 grms. per litre are added, the volume of the liquid is made up to 100 cc., and it is examined with a Féry spectrophotometer.

MISCELLANEOUS.

Faraday Society.—A joint meeting of the Faraday Society and the Local Section of the Society of Chemical Industry will be held at Manchester on Friday evening, April 4th, 1913. The meeting will take the form of a General Discussion on "The Corrosion of Iron and Steel." Members desirous of contributing papers to the Discussion or otherwise taking part therein are requested to communicate at once with the Manchester Local Honorary Secretary of the Faraday Society, Prof. W. W. HALDANE GEE, The Municipal School of Technology, Manchester.

Franklin Institute.—Awards of the Elliott Cresson Gold Medal.—The Franklin Institute, acting through its Committee on Science and the Arts, recently awarded the Elliott Cresson Gold Medal, the highest in the gift of the Institute, to the following gentlemen :—

Charles Proteus Steinmetz, A.M., Ph.D., of Schenectady, New York, in recognition of successful application of analytical method to the solution of numerous problems of first practical importance in the field of electrical engineering.

Emile Berliner, of Washington, D.C., in recognition of important contributions to telephony and to the science and art of sound reproduction.

Isham Randolph, D.Eng., of Chicago, Ill., in recognition of distinguished achievement in the field of civil engineering.

John William Strutt, Baron Rayleigh, P.C., J.P., D.C.L., LL.D, F.R.S., Hon.C.E., Sc.D., of Witham, Essex, in recognition of extended researches of signal importance in physical science.

Sir William Ramsay, K.C.B., LL.D., D.Sc., M.D., Ph.D., F.R.S., F.C.S., of London, in recognition of numerous discoveries of far reaching importance in the science of chemistry.

Emil Fischer, Ph.D., M.D., D.Sc., F.R.S., of Berlin, Germany, in recognition of numerous contributions of fundamental importance to the science of organic and biological chemistry.

THE CHEMICAL NEWS.

VOL. CVII., No. 2782.

THE LIFE NUTRIENT IN FOODS.

By ERNEST L BRIGGS.

RE-WRITE your works on foods, Mr. Langworthy and Dr. Wiley! Begin anew your nutrient studies, Uncle Sam, and you dietetic experts in college, State Departments, of Agriculture, Food Commissions, and Government, State, and City Laboratories, for all your labour has been for nothing. You have reckoned on a wrong basis. Your premises being wrong your conclusions are wrong. You might as well admit it now as later, that you know nothing at all about the nutritive properties of foods, for that is just what it amounts to in the light of the latest revelation. And this is not said in sarcasm either.

From Chicago is winged the aviso that is to fall like a bomb in the ranks of the food experts, exploding all their cherished theories. It is nothing more nor less than the discovery of the life-substance in foods. "Trophogen" is its name. Rutledge Rutherford is its discoverer. It is the most important discovery that has been made in the history of alimental science.

For years this Chicago physiologist has been searching for what he finally has found. The victory came as a climax to a long series of experiments on guinea-pigs, mice, chickens, and kittens. Only after repeated failures did Rutherford finally succeed in locating and identifying the remarkable substance he has named Trophogen (from the Greek, *Trepho*, to nourish, plus *gennao*, to produce, meaning nutriment producing). Trophogen is made the basis of a new science called Trophology. It is the all-containing nutrient of foods. With it extracted from the diet, the animal subjects soon starved to death. By successive manipulation Rutherford was able to increase or decrease the nutritive value of the food merely by adding too or lessening the amount of Trophogen. He learned that Trophogen was both the life-producing and the flesh-forming substance of all foods. The vital energy principle of Trophogen is called Biogen; the tissue-making, Sarcogen. Hence it possesses all the essentials of life and bodily sustenance, and is declared to be the one and only nutrient in any food. Without it food is not food; with it in sufficient quantity, any food is life-sustaining.

A very pretentious branch of the United States Department of Agriculture—the Office of Experiment Stations—is devoted to food experiments. It spends millions in analysing foods, compiling dietary standards, and tabulating food values. About all the foods of American consumption—some four or five thousand of them—it has listed in its tables. This same government office is the fountain source of all the information that guides our domestic science schools, our household economics, clubs, and cookery schools, and dietetic writers. Its tables, formulas, and standards tell us just how the fats, proteins, and carbohydrates shall be apportioned in order to sustain life and health; just what a man at moderate muscular work should eat; what the proper ration for one at hard work, or at sedentary occupation; for women and for children of all ages; diets for hot and cold climates are prescribed, for summer and winter, and enough literature to fill a library has issued from this bureau for our information. It has all been misinformation. Not a standard, not a table, not an item is correct in the light of the newest discovery. Here is the truth about foods as revealed in the science of Trophology.

Trophogen, the all-sustaining nutrient, is most plentiful in albuminous foods. The so-called protein, originally believed to be obtained as a distinct substance from albumen, fibrine, and casein, and to be the basis of animal tissue, is simply alkali albumen.

Sugar and starch foods, commonly called carbohydrates, are considerably lower in Trophogen than are the albuminoids. There is no basis of fact in the theory that fats and carbohydrates excel as heat and energy producers. Their food value depends entirely on their Trophogen contents.

Pure fats, unmixed with other substance, contain no Trophogen.

Climate and temperature have no bearing on the kind of food required, for there is but one food substance, and that is Trophogen.

Variety or monotony in diet counts for nothing, except in cases where the system has become so accustomed to one or the other that a change from the customary diet would upset the digestive organism.

Chemical preservatives rob food of Trophogen, and therefore are civilised man's greatest enemies in the struggle for existence.

In some manufacturing processes parts of food richest in their Trophogen contents are cast off either for the purpose of keeping the food from spoiling or for the sake of appearance, as in the grinding of wheat and corn into flour and the polishing of rice.

Fresh foods are always most healthful, because the quantity of Trophogen lessens with the age of garnered foods.

Trophogen is produced exclusively by the vegetable kingdom, though it is retained by the animal flesh, which often supplies it in a more concentrated and digestible form than the vegetable food.

Revolutionary are the dicta indeed; yet they explain many hitherto perplexing problems. They unravel the mystery of the Brooklyn grass-eater, the man who regained his health from a grass diet and continued to thrive on it. They explain why fruits and salads are healthful despite the fact that the Government experts classify them so very low in the scale of food nutrients. Our experts have declared that no person could eat any particular kind of food for a long time and retain his health; that to eat an egg or a quail every day for three months, for instance, would mean certain death. Trophology explains why it has been so easy to disprove such ridiculous postulates. The foods in question contain Bitrophon, and that was all that was necessary.

To the new student in dietetics all along the first problem has been, how in the world people ignorant of dietetics managed to live at all. Still we found that they did live, and that many of the ignorant ones enjoyed better health than some of the experts. Trophology makes the reason plain. The difference between Trophology and dietetics is this:—

Trophology explains why, and does not attempt to tell how; it teaches of the origin, the nature, the cause and effect of food nutriment.

Dietetics attempts to prescribe rules for diet, and to determine the quantity and quality of rations best adapted for human sustenance.

Trophology is a true science, yet a person can enjoy just as good health, and get along just as well generally without it as with it. Dietetics is not a science, and a person cannot get along as well with it as without it. He is worse off for knowing it than for not knowing it.

Dietetics taught that carbohydrates were dangerous in summer time and in warm climates, yet we found them being eaten in the hottest weather, even in the tropics, quite as extensively as in the winter and the north. It taught that we ought to have a very varied and mixed diet so as to supply the proper ratio of proteins to the fats and carbohydrates; yet we saw the Chinese, the Japanese, and the natives of India living almost exclusively on a rice diet. And, further, the records show:—

"The roving Indian of the plains, who lives almost exclusively on unsalted meat; the Polynesian, who was accustomed for eight months in the year to make his meal

from bread-fruit; the Central American natives, whose bill of fare scarcely ever went beyond maize; and the Scotch peasant, who in former years tasted nothing but oatmeal six days out of seven, were all examples of conspicuous bodily vigour nourished by almost a single article of diet quite different in each case." Other examples are numerous.

Prof. Rutherford quotes the incidences to prove his aphorism that variety or monotony in diet counts for nothing. He is careful to explain, however, that monotony of the kind mentioned might prove harmful to one accustomed to a varied diet, but not more so than a varied diet would be to one accustomed to any kind of monotony.

Alexander von Humboldt observed that the South American Indians suffered great impairment in health when removed to parts where they could not obtain the uniform sustenance to which they had been accustomed. Similar observations are made by Darwin and Sir John Lubbock.

All such cases must have been enigmas to the former school of physiologists, if they ever stopped to learn about them. Trophology makes them clear, merely the natural thing to be expected, for it shows that any food that supplies sufficient Trophogen or Bitrophon, the two words being synonymous, contains all the essentials of life.

Vegetables ought to be most healthful in warm climates and hot weather, and meat in northern climates and cold weather, according to dietetics, and we have been taught this so long that we actually believe it true. The only reason for the assumption, however, is that vegetables are eaten more extensively in hot climates than in cold, and meat more extensively in cold climates, but the reason is the greater abundance or accessibility of the different foods to the respective localities. As to the theory of the different adaptabilities of the vegetable and meat diets, it lacks all elements of proof.

"A vegetable or a meat diet is as healthful at the poles as at the equator," said Prof. Rutherford. "It makes no difference which is eaten so long as the Trophogen is there, and there is but one kind of Trophogen. The reason the Esquimo does not eat more vegetables is because he cannot get them, not because he does not like them. He does not select his meat diet from choice but from necessity. The fondness of the Esquimo for fat has been ridiculously exaggerated. The fact is he does not prefer fat, but eats it along with the rest of the meat for the sake of economy. Likewise he also eats putrid meat, not because he prefers it to fresh, but because it often is all he can get. From long ages of existence in a climate where only animal food is obtainable, and that scarce at certain seasons, the Esquimo has gradually acquired a tolerance for such foods, and they are not so repugnant to him as to us for this reason. The Peary arctic expedition brought back the information that natives of the coldest climates are ravenously fond of vegetables, and when canned corn, tomatoes, peas, dried beans, and cereals were offered, they ate of them greedily. The tallow candle fable of the Esquimo in Paris is largely responsible for the "scientific" conclusions as to their fondness for fat.

"The Hindu does not choose boiled rice and ghee (melted butter) because of any dietetic enlightenment. Neither is this the cause of the monotonous rice diet of the Chinese and Japanese coolies. In fact these people know nothing about the science of dietetics. They eat the foods because they are most plentiful and accessible.

"Inhabitants of the tropics are lovers of meat. Under the burning sun of the equator meat is eaten with a relish when it can be procured, and no ill effects result. So fond of meat are the natives of equatorial Africa that they will devour it when in an advanced stage of decomposition. The experience of our workmen in the Panama canal zone has proved that a mixed diet of meat and vegetables is most healthful for them, not because the climate requires it, but because they were accustomed to a mixed diet at home. So when their food was of both meat and vegetables they suffered less from abdominal complaints. But to recount the many absurdities of our dietetic theories would fill a volume. The wonder of it is that they should be held to so tenaciously when they are so easily disproved.

"It is quantity and not quality of food that counts, provided it possess the requisite amount of Trophogen. One of the most harmful and ridiculous of the prevailing postulates is that stinted rations are best for brain workers.

"Show me a race of people forced to subsist on stinted rations and I will show you a people low in the scale of the human species. The pigmy tribes of Africa are examples. All of them inhabit regions where food is scarce and hard to procure. Most of them rarely ever taste any flesh foods, because they have such meagre means of procuring it. There are the Akka pygmies of the Wells River region, beyond the Niam-Niam country, who have been half starved for ages; the Congo pygmies, recently discovered by Colonel James J. Harrison, of Yorkshire, England; the pygmy tribes of Tapiero, an ill-fed, half-human people, some of whom were run down and captured like beasts by the recent British expedition to Dutch Guinea. There are the Bushmen, ill-nourished from the scanty sustenance afforded by the Kalahari desert; the Fuegians, living on the scanty supply of seaweed of the West Coast of Terra del Fuego, declared to be the most degraded of savages; and nearly everywhere it is the same—a low food supply with a low grade of people. The semi-human dwarfs of Tapiero, Africa, have their capital at Wambrini, on the southern slope of the low-lying hills, 1800 feet above sea-level. Their average height is 4 ft. 8¾ in. Ten miles away in the fertile district of the Tuaba river live the Papuans, a well-developed tribe with an average height of 5 ft. 6¾ in. Both are of the same original stock, the former having become dwarfed in mind and body from the food scarcity. The Papuans subsist almost entirely on sago and fish, with flesh on such rare occasions as it can be obtained. Tribes of the same race as the impoverished Bushmen inhabit the bounteous lands south of Lake Ngomi, and show fine stature and advanced intellect. The splendid Araucacians of Southern Chile, who are never in want, are of the same parent stock as the wretched, dwindled Fuegians south of them. Not variety but abundance of food determines the superiority of races. Civilised races gained the ascendency because of their ability to protect themselves against food scarcity. Their first step towards this end was the adaptation of their constitution to subsist on nearly any kind of food.

"Of course some foods are richer in Trophogen than others, but in such cases it simply takes more food to satisfy. That is all. The people who can get the Bitrophon or Trophogen in the most concentrated and accessible form, however, have much the advantage. Bark, leaves, and all living wood contain Trophogen, but the tough fibre renders it inaccessible."

A quiet and unassuming man is Prof. Rutherford. A physiologist and a student, most of his time is spent in research and experimentation. Very little has been known of him before, save that he edits *The National Food Magazine* and was a loyal supporter of Dr. H. W. Wiley while he was head of the government chemistry bureau. His articles on "Cells and the Upbuilding of Body Tissue," and "Food in its Relation to the Human Body," have attracted considerable attention. But the world will know more of him later. His disclosures are sure to turn everything topsy-turvey in the food world. All our physiologies must be revised, the study of foods begun all over again, and a few more words added to the lexicon. As Newton overturned old traditions by revealing the law of gravitation; as radio activity has upset all previous calculations concerning the make-up of matter, so has Trophogen, or Bitrophon, set at naught all our former reckonings regarding the nutritive power of foods.

Several important disclosures led up to the discovery of the life substance in foods. While Rutherford was busily

engaged in his researches, hunting for the then unknown substance, his confidence in the existence of such a substance was greatly strengthened by the experiments with rice in relation to the disease "berri-berri." Here it was shown that polished rice was a contributing cause of the affliction. This fact being fairly determined all manner of experiments were made in the preparation and feeding of the cereal. In these it was shown that Fats, Proteins, Carbohydrates, and Ash could all remain in the rice, and still it would be deficient in nutrition, or rather conducive to the disease. Undoubtedly some essential constituent of the rice had been removed in the polishing. Also in white flour a somewhat similar deficiency was noted, causing the belief that the milling and bleaching process had removed some valuable nutrient. There must be a life sustenance in the foods as yet unknown.

Experiments conducted by Prof. F. G. Hopkins, of Cambridge University, along different lines, pointed to the same conclusion. Prof. Hopkins was studiously engaged in his experiments when Prof. Stepp, of Germany, announced the discovery of a substance he named Lipoid, which discovery, up to that time, was the most important step in the solution of the mooted problem. The conclusions of the Cambridge professor that there was a vital substance in foods which none had yet discovered was made known a short time ago. That he was running the Chicago editor a close race for the honour of the discovery of Trophogen is plainly shown by the text of his report. It indicates that he was nearer the solution of the problem than he himself had realised.

Alfred W. McCann, of New York, found that the treatment of many cereals in the manufacture was the cause of certain degenerative diseases. This discovery in itself would have been an important step in the right direction if Mr. McCann had not prematurely concluded that Ash (mineral salt) alone was the element omitted from the foods. It was the lessened quantity of Trophogen in the foods that impaired their nutritive value.

Dr. James R. Mitchell also discovered that the absence of a certain nutriment in foods produced nerve twitching. Experiments made by Voit, in Leipsic, revealed that there was the absence of something in certain foods that caused pigeons to show weakening and thinning of the skull even to the extent of perforation.

These facts convinced the more observing that ordinary food products contained a certain unknown constituent far more important than all others. What then could the constituent be? The observers knew that it was present only in minute quantities, but its exact identity they could not determine. Few there were who realised it was the very life element of the foods they were looking for. Their fondest hopes was to discover another, but very important, nutrient to add to the already lengthened list.

Trophogen is not a Protein, nor Carbohydrate, nor Ash, yet it is all there is in food that is nutritious. It resembles fat in that it is soluble in organic solvents, yet it is not fat, nor even related to it. It is a very subtle substance, generally containing carbon, hydrogen, nitrogen, and phosphorus.

Of the successive disclosures which led up to the discovery of Trophogen, Prof. Rutherford gives first place to Prof. Stepp's Lipoid. "But for the discovery of Lipoid," he said, "it is doubtful if ever I would have been successful in my search for Trophogen. Lipoid furnished a stepping-stone by which I was able to peer deeper into the hidden mysteries of food nutrition.

Rutherford began his experiments in 1908 with guinea-pigs as subjects. They proved so frail that they died when only a small part of the food nutrient had been extracted. Next he tried mice. These too suffered abnormally from the impairment of the nutriment and from handling and confinement. Finally, as a last resort, he tried kittens. With these he carried his experiments to a successful conclusion.

Mice were the subjects in Prof. Stepp's experiments. They were well suited for the Lipoid tests, but never would have sufficed to detect the very subtle Trophogen. In the first test the mice were given a dried mixture of rice, very rich in protein and milk. On this they thrived. By the use of alcohol and ethers he then extracted all the food nutrients from the mixture. The residuum had all the appearance of the integral, but it possessed no substance whatever, and the mice that were fed on it soon starved to death. When the evaporated extract was returned the vitality of the food was instantly restored, and it proved as wholesome to the mice as before. This extract is what Prof. Stepp termed Lipoid. It seems to be identical with Rutherford's Sarcogen, the flesh-element of Bitrophon. Rutherford's experiments showed that kittens would starve to death when either the flesh-nutrient Sarcogen (Lipoid), or the life substance (Biogen) was extracted from the food. When the Sarcogen was extracted, however, the kittens showed marked and rapid emaciation. Death followed much quicker when the Biogen was extracted, but there was no noticeable emaciation. The Sarcogen and Biogen were always found united together in the outer wall of all protoplasmic cells, combining to form the substance Trophogen. From these facts it was plain to infer that Trophogen was the one and only nutrient of all foods. Repeated experiments on many different kinds of subjects and careful chemical analyses of the substances positively confirmed the conclusion.

(To be continued).

ON A RELATION BETWEEN THE BOILING-POINTS AND MOLECULAR WEIGHTS OF THE MEMBERS OF HOMOLOGOUS SERIES.

By S. SUGDEN.

IN the CHEMICAL NEWS (1912, cvi., 187) it was shown by J. C. T. that for certain groups of elements and trichlorides the boiling-point was proportional to the square root of the molecular weight. The writer had been working on the boiling-points of the members of a homologous series, and had obtained a similar formula in some cases, notably the paraffins. This was discovered for the paraffins by Walker in 1894 (*Journ. Chem. Soc.*, lxv., 193). In other cases another term depending on the molecular weight has to be introduced, as would be expected from Van der Waal's equation:—

$$\left(P + \frac{a}{V_2}\right)(V - b) = RT.$$

This may be written—

$$PV + \frac{a}{V} - Pb - \frac{ab}{V_2} = RT.$$

Liquefaction will take place when the internal attraction of the particles for each other surpasses a critical value; *i.e.*, when $\frac{a}{V_2} = K$.

$$\therefore V = \sqrt{a/K}.$$

Combining this with (1) we have—

$$\frac{P\sqrt{a}}{\sqrt{K}} + \sqrt{aK} - Pb - Kb = RT,$$

where T is the boiling-point at the pressure P.

Thus at constant pressure the boiling-point $T = \alpha\sqrt{a} - \beta b$; where α and β are constants.

Now, a is the coefficient of attraction between the molecules, and is therefore proportional to their mass M. b is probably also a function of M whose value will vary with the class of substances under consideration. For members of a homologous series it may obviously, as a first approximation, be considered to vary as M.

Thus the boiling-points of the members of a homologous series should be connected by the relation:—

$$T = A\sqrt{M} - BM \quad . \quad . \quad . \quad . \quad . \quad . \quad 2,$$

where A and B are constants for the series, and M is the molecular weight.

If B is small compared with A, this reduces to the formula found by J. C. T. for certain elements. This formula holds for the paraffins, with the exception of the first few members, as is shown in Table I., and for the ethers, Table V.

In the case of the fatty acids, however, $\frac{T}{\sqrt{M}}$ is not constant, but decreases as the molecular weight rises. By applying the extended Formula 2 a constant value for A is obtained, as is shown in the last column of Table II.

The methyl esters of the fatty acids give an intermediate result, but a more satisfactory constant is obtained by the use of the second formula, Table III.

The paraffins and acids here considered are the normal members of the series, and it has been shown that their boiling-points fit in fairly well with the formula—

$$T = A\sqrt{M} - BM.$$

This is obtained on the hypothesis that the volume of the molecules is proportional to their mass. This is obviously true in the case of straight chain hydrocarbons, but in the isomeric compounds some other function of M will have to be substituted for M. The general form of the equation being—

$$T = A\sqrt{M} - Bf(M).$$

This formula may, perhaps, be made to account for the boiling-points of the isomers of these compounds, but up to the present the writer has not been able to find a satisfactory function of M.

Tables for alcohols, aldehydes, and ketones are also appended.

TABLE I.—*Normal Paraffins.*

Formula.	M.	$\sqrt{M}$.	T° abs.	T/$\sqrt{M}$.
CH_4 ..	16	4·00	109	27·2
C_2H_6 ..	30	5·48	160	29·2
C_3H_8 ..	44	6·63	235	35·5
C_4H_{10} ..	58	7·62	274	36·0
C_5H_{12} ..	72	8·48	309	36·5
C_6H_{14} ..	86	9·27	342	36·8
C_7H_{16} ..	100	10·00	371	37·1
C_8H_{18} ..	114	10·68	398	37·2
C_9H_{20} ..	128	11·31	423	37·4
$C_{10}H_{22}$ ..	142	11·92	446	37·5
$C_{11}H_{24}$ ..	156	12·53	468	37·3
$C_{12}H_{26}$ ..	170	13·04	487	37·3
$C_{13}H_{28}$ ..	184	13·57	507	37·4
$C_{14}H_{30}$ ..	198	14·08	525	37·3
$C_{15}H_{32}$ ..	212	14·56	543	37·3
$C_{16}H_{34}$ ..	226	15·03	560	37·3
$C_{17}H_{36}$ ..	240	15·49	576	37·1
$C_{18}H_{38}$ ..	254	15·94	590	37·0
$C_{19}H_{40}$ ..	268	16·37	603	36·8
			Mean	37·2 ± 0·04

TABLE II.—*Normal Fatty Acids.*

Formula.	M.	$\sqrt{M}$.	T° abs.	T/$\sqrt{M}$.	T/$\sqrt{M}$+2·0$\sqrt{M}$. A =
CH_2O_2..	46	6·78	374	55·2	68·8
$C_2H_4O_2$.	60	7·75	391	50·5	66·0
$C_3H_6O_2$.	74	8·60	414	48·1	65·3
$C_4H_8O_2$.	88	9·38	435	46·3	65·1
$C_5H_{10}O_2$	102	10·10	462	45·7	65·9
$C_6H_{12}O_2$	116	10·77	473	43·9	65·4
$C_7H_{14}O_2$	130	11·40	496	43·5	66·1
$C_8H_{16}O_2$	144	12·00	509	42·4	66·4
$C_9H_{18}O_2$	158	12·57	527	41·9	67·0
$C_{10}H_{20}O_2$	172	13·12	541	41·2	67·9
$C_{11}H_{22}C_2$	186	13·64	550	40·3	67·5
			Mean		66·5 ± 0·2

TABLE III.—*Methyl Esters of the Fatty Acids.*

Ester.	M.	$\sqrt{M}$.	T° abs.	T/$\sqrt{M}$.	T/$\sqrt{M}$+0·5$\sqrt{M}$.
Methyl—					
Formate..	60	7·75	305·5	39·4	43·3
Acetate ..	74	8·60	330·3	38·4	42·7
Propionate	88	9·38	352·5	37·6	42·3
Butyrate .	102	10·10	375·3	37·2	42·2
Valerate .	116	10·77	400·3	37·2	42 6
Hexoate .	130	11·40	422·6	37·1	42·8
Heptoate	144	12·00	445·1	37·1	43·1
Octoate ..	158	12·57	465·9	37·1	43·4
			Mean	37·6 ±0·2	42·8 ±0·1

TABLE IV.—*Alcohols.*

Formula.	M.	$\sqrt{M}$.	T° abs.	T/$\sqrt{M}$.	T/$\sqrt{M}$+4·4$\sqrt{M}$.
CH_3OH .	32	5·66	339	59 9	84·8
C_2H_5OH	46	6·78	351	51·8	81·6
C_3H_7OH	60	7·75	370	47 7	81·8
C_4H_9OH	74	8·60	390	45 3	83·1
$C_5H_{11}OH$	88	9·38	411	44·0	85·3
			Mean		83·3 ± 0·5

TABLE V.—*Ethers.*

Formula.	M.	$\sqrt{M}$.	T° abs.	T/$\sqrt{M}$.
C_2H_6O ..	46	6·78	249	36·7
$C_4H_{10}O$ ..	74	8·60	308	35·8
$C_6H_{14}O$ ..	102	10·10	364	36·0
$C_8H_{18}O$ ..	130	11·40	414	36·3
$C_{10}H_{22}O$ ..	158	12·57	443	35·2
$C_{16}H_{34}O$ ..	242	15·56	553	35·5
			Mean	35·9 ∓ 0·15

TABLE VI.—*Aldehydes.*

Formula.	M.	$\sqrt{M}$.	T° abs.	T/$\sqrt{M}$.	T/$\sqrt{M}$+ $\sqrt{M}$.
HCHO ..	30	5·48	252	46·0	51·5
CH_3CHO .	44	6·63	294	44·3	50·9
C_2H_5CHO	58	7·62	322	42·3	49·9
C_3H_7CHO	72	8·48	347	40·9	49·4
C_4H_9CHO	86	9·27	375	40·4	49·7
$C_5H_{11}CHO$	100	10·00	401	40·1	50·1
$C_6H_{13}CHO$	114	10·68	428	40·0	50·7
			Mean		50·3 ± 0·2

TABLE VII.—*Ketones.*

Formula.	M.	$\sqrt{M}$.	T° abs.	T/$\sqrt{M}$.	T/$\sqrt{M}$+ $\sqrt{M}$.
$(CH_3)_2CO$.	58	7·62	329	42·8	50·4
$(C_2H_5)_2CO$	86	9·27	376	40·6	49·9
$(C_3H_7)_2CO$	114	10·68	417	39·0	49·7
$(C_4H_9)_2CO$	142	11·92	—	—	—
$(C_5H_{11})_2CO$	170	13·04	503	38·6	51·6
			Mean		50·4 ± 0·3

Animal Fats and Petroleum Jelly in the Treatment of Leather.—As a natural lubricant for leather, animal fats render it soft and pliable, but tend to permeability by moisture. Occasional treatment with them acts as a preservative, but for use petroleum jelly immediately applied by friction, using only small quantities, tends to render it waterproof, and in giving it gloss and finish renders it of itself an efficient polish. Again, with morocco leather petroleum jelly applied as above is particularly useful in facing it up and giving it finish. In the latter case it should be applied by dabbing the surface and careful friction.—J. C. THOMLINSON, B.Sc.

SOME RELATIONS BETWEEN CATHODE AND RÖNTGEN RAYS.*

By R. WHIDDINGTON, M.A., D.Sc.,
Fellow of St. John's College, Cambridge.

Physicists have long felt the need of being able to define without ambiguity the quality of a beam of Röntgen rays in terms of some easily measured variable. If it were as easy to measure the wave-length of Röntgen rays as it is in the case of ordinary light, there would be no difficulty about the matter; but as we are at present only able to say that the wave-length of Röntgen rays—if, indeed, they *are* waves—is exceedingly small, it is obviously out of the question to try and make the wave-length our basis of experimental measurement. For many years workers in this field have defined the quality of their rays in terms of the absorption suffered by them in passing through a standard material, usually aluminium. Some experiments carried out by the writer during the past year or two have suggested an alternative (or additional) method which makes use of the fact that the quality (or hardness) of a beam of rays from a focus bulb is determined by the velocity of the cathode rays striking the anticathode.

Adopting this plan, we could say of any given homogeneous beam of Röntgen rays—this beam would be produced by a stream of cathode particles of such and such a velocity on striking an anticathode.

This mode of definition leads to very interesting and simple results in the case of the fluorescent radiations discovered by Prof. Barkla. A radiation of this type is emitted by an element when suitably stimulated, its quality (as measured by the distance it can penetrate in aluminium) being determined solely by the nature of the radiating element. The higher the atomic weight of the element the more penetrating its fluorescent radiation. Now suppose that we have a slab of an element of atomic weight M and illuminate it with a focus bulb. Experiment shows that if the bulb is at first very soft and is gradually allowed to harden up, the slab of M will not emit its fluorescent radiation (which, let us say, can penetrate just 1 cm. of aluminium) unless the radiation from the bulb can penetrate ever so little *more* than 1 cm. of aluminium. Thus, if our bulb is in that state of hardness as just to excite the fluorescent radiation of M we can say of the mixed beam emitted by the bulb that the hardest constituent is the same as the fluorescent radiation from M. Now experiment shows further that the velocity of the cathode rays within the bulb at this stage is equal to $M \times 10^8$ cm./sec. We therefore see that the fluorescent radiation of M would be the same as the hardest rays from a focus bulb in which the cathode rays were moving with a speed of $M \times 10^8$ cm./sec.; *e.g.*, the speed for copper of atomic weight 63 would be $6{\cdot}3 \times 10^9$ cm./sec., a velocity which would be attained when a potential of 11,000 volts is applied to the terminals of the tube.

Quite recently Barkla has shown that elements of high atomic weight emit *two* fluorescent radiations. A formula accounting for this second "line in the fluorescent spectrum" is $\frac{1}{4}(M-48) \times 10^8$ cm./sec., which gives us the minimum cathode ray speed required to excite the second and softer radiation, *e.g.*, the element bismuth, whose atomic weight is 208, emits two "lines" determined by the cathode ray speeds: $M \times 10^8 = 2{\cdot}08 \times 10^{10}$ cm./sec. and $\frac{1}{4}(M-48) \times 10^8 = 8{\cdot}0 \times 10^9$ cm./sec. The former giving the "harder," the second the "softer" line in the spectrum. Relations similar to the above are found to hold when we study the secondary cathode particles emitted from a metal surface stimulated by Rontgen rays. If the two radiations from a fluorescing element of atomic weight M fall on a material surface, two sets of cathode particles spring out, one set having a speed of $M \times 10^8$ cm./sec., while the other set have a speed of $\frac{1}{4}(M-48) \times 10^8$ cm./sec.

These results lend support to the views of Prof. Bragg, who regards Röntgen rays as localised bundles of energy travelling through space rather than pulses which must inevitably spread out and distribute their energy. Friedrich Knipping and Laue, however, have recently succeeded in showing that a crystal treats Röntgen rays in exactly the same way as a diffraction grating treats light, *i.e.*, produces a Röntgen ray spectrum. Thus, one set of experiments indicates that Röntgen rays are waves in the ether, while another set indicates that they are not. Röntgen rays, in fact, are still X-rays. There is reason to think, however, that any beam of Röntgen rays is a mixture of these two kinds of radiation.

* Abstract of a Paper read before the Röntgen Society, January 7th, 1913.

ON THE NITRILE OF FUMARIC ACID AND THE PREPARATION OF METHYL MALEATE.

By EDWARD H. KEISER and L. McMASTER.

In the synthesis of fumaric and maleic acids from acetylene by means of the iodides and potassium cyanide the nitriles of the acids were not isolated. Subsequently, E. H. Keiser and J. J. Kessler (*Am. Chem. Journ.*, xlvi., 523) obtained the nitrile of fumaric acid by heating fumaramide with phosphorus pentoxide. The long slender needles that formed as a sublimate undoubtedly had the composition of fumaric nitrile. They had a pleasant odour, and when treated with alkalis gave off ammonia. In short, the behaviour of the substance was such as one would expect from a cyanide. Difficulty was experienced, however, in trying to convert the fumaric nitrile into fumaric acid. This was no doubt due to the fact that the quantities worked with were small. We have now prepared the nitrile in larger quantities, and have succeeded in converting it back into fumaramide and into fumaric acid, thus establishing, beyond all doubt, its constitution.

This conversion was found to take place readily by means of an alkaline solution of hydrogen dioxide (*Ber.*, xviii., 355), the action taking place according to the equation:—

$$\begin{matrix} CHCN \\ \| \\ CHCN \end{matrix} + 2H_2O_2 = \begin{matrix} CHCONH_2 \\ \| \\ CHCONH_2 \end{matrix} + O_2.$$

The fumaramide thus formed was then transformed into fumaric acid by warming with dilute caustic potash.

Twenty-five hundredths grm. of fumaric nitrile was treated with 25 cc. of a 3 per cent solution of hydrogen dioxide, and the liquid made faintly alkaline with a few drops of caustic soda solution. There was a rapid evolution of oxygen, and after a short time a white precipitate separated. This was removed by filtration, and was found to be insoluble in cold water, in alcohol, and ether, but was soluble in hot water, thus showing the properties of fumaramide. In determining the melting-point, it became black at 232°, and melted completely at 267°. For the sake of comparison a sample of fumaramide was prepared from diethyl fumarate by the action of ammonia, and this behaved in the same way as that obtained from the nitrile. The melting-point of fumaramide is given by Curtius and Koch at 232° "with carbonisation" (*Journ. Prakt Chem.*, [2], xxxviii., 478). Hell and Poliakow (*Ber.*, xxv., 643) give it at about 266°. With a second specimen of the fumaramide made from the nitrile we found that at 233° the substance became black, and at 267° it melted sharply.

The fumaramide thus made from fumaric nitrile was then hydrolysed by warming upon the water-bath for one hour with dilute caustic potash. All odour of ammonia was then gone, and the solution was allowed to cool, and was then neutralised with dilute nitric acid. Silver nitrate was added, and a white precipitate of silver fumarate was formed. This was filtered, washed, and dissolved in dilute ammonia, and re-precipitated by again neutralising with nitric acid. The precipitate, after filtering and

washing, was dried at 100°. On analysis the following result was obtained :—

0·0628 grm. substance gave 0·543 grm. AgCl.

	Ag.
Calculated for $C_5H_2O_4Ag_2$	65·4
Found	65·1

The dried salt deflagrated like gunpowder when heated, this being one of the characteristic properties of silver fumarate. It was also insoluble in boiling water, a fact which distinguishes it from silver maleate.

Another portion of fumaramide made from the fumaric nitrile by means of hydrogen dioxide was saponified by alcoholic potash. As the amide is only slightly soluble in absolute alcohol, the solution was boiled for sixteen hours. It was then filtered and evaporated to remove the alcohol, water added, and the alkali neutralised with nitric acid. The silver salt was then precipitated, washed, dried, and analysed.

0·1016 grm. substance gave 0·0877 grm. AgCl.

	Ag.
Calculated for $C_4H_2O_4Ag_2$..	65·4
Found	65·0

Dimethyl Maleate.—This ester has heretofore been made by the action of methyl iodide upon silver maleate. We have succeeded in preparing it from methyl alcohol, maleic acid, and sulphuric acid. Five grms. of maleic acid, 50 cc. of methyl alcohol, and 2 cc. of concentrated sulphuric acid were boiled for four hours under an inverted condenser. The liquid was then poured into an evaporating dish, and the alcohol allowed to evaporate. The residue was stirred up with barium carbonate, and allowed to stand in contact with it for several days. Ether was added to the mixture, and the solid matter separated by filtration. The ether was removed from the filtrate by evaporation, and the thick oily residue, consisting of dimethyl maleate, was distilled. Its boiling-point was found to be 203°. A small quantity of a solid melting at 102° was found in the condenser; this was dimethyl fumarate. That the clear distillate was dimethyl maleate was proved by adding bromine water to a portion of it. On standing, a white solid crystalline compound was obtained. This was re-crystallised from its solution in ether. It melted at 102°, and had all of the properties of dimethyl fumarate.

We have also studied the action of ammonia upon dimethyl maleate. When a mixture of the ester and ammonia solution was allowed to stand several days, the oil gradually dissolved, but no precipitate of amide was formed as in the case of the dimethyl fumarate. On evaporating slowly, after the ammonia and water were removed, a thick yellowish oil remained, which became semi-solid when it was stirred, and was very difficult to detach from the platinum dish in which it was contained. A portion of it, when heated, acquired a red colour. Another portion, when mixed with phosphorus pentoxide, gradually became hot, and as the mass turned black a white sublimate came off which was condensed in an inverted funnel. This sublimate melted at from 135° to 138°, and may have been the nitrile of maleic acid. A third portion was warmed with caustic soda, and ammonia was given off. In all probability this thick glue-like mass was the amide of maleic acid.—*American Chemical Journal*, xlix., No. 2.

Preservation of Phenylhydrazine Reagents and Osazones.—G. Denigés.—It is well known that phenylhydrazine reagents, used to characterise aldoses and ketoses, very rapidly undergo oxidation and become useless, while the osazones alter even more quickly. The author has found that the addition of a small quantity of alkaline bisulphite preserves both phenylhydrazines and osazones, the quantity added being about 1 drop of sodium bisulphite solution (30—36° Baumé) to 1 or 2 cc. of the reagent.—*Bulletin des Travaux de la Société de Pharmacie de Bordeaux*, lii., 513.

THE PRODUCTION OF LIGHT BY CHEMICAL ACTION.

By J. H. VINCENT, M.A., D.Sc., and J. MARLEY, B.Sc., London County Council Paddington Technical Institute.

MATUSCHEK and Nenning (*Chem. Zeit.*, 1912, xxxvi., 21) find experimental evidence which they interpret as proving that chemical action is accompanied by the evolution of light capable of affecting a dry plate, even in those cases in which light is not visibly emitted. We have tried many experiments on the same lines as those described by these authors. At first some slight photographic effects were noted which could not be traced to known chemical action of the kind studied by Russell, and which is attributed to hydrogen peroxide. These positive results disappeared as experience was gained in protecting the photographic plate from the action of extraneous light. As some of the experiments have lasted several weeks, the precautions against the accidental entry of light to the plate cannot be too elaborate. In all cases any vapours, &c., arising from the substances engaging in the chemical action must also be prevented from acting on the plate. Apart from the Russell effect due to metal screens, &c., we have been unable to find any evidence of action on the plates.

The reactions tested were :—

1. Action of sulphuric acid on zinc.
2. Action of hydrochloric acid on sodium-metasilicate.
3. Action of nitric acid on lead.
4. Hardening of plaster of Paris.
5. Electrolysis of water with platinum electrodes.

It is difficult to account for the positive effects observed by Matuschek and Nenning. Properly controlled experiments with vessels containing water heated electrically and with paraffin wax heated electrically, have convinced us that the heat produced by chemical action is not competent to account for the apparent positive results. We find then no evidence of any radiation capable of acting on a photographic plate after passing through glass.

THE IODIC ACID PROCESS FOR THE DETERMINATION OF BROMINE IN HALOGEN SALTS.*

By F. A. GOOCH and P. L. BLUMENTHAL.

THE oxidation potential of a solution of chlorine in potassium chloride and water is, according to Bancroft (*Zeit. Phys. Chem.*, x., 405), about 0·241 volt higher than that of a solution of bromine in potassium bromide and water. Iodic acid has an oxidation potential 0·064 volt higher than that of an equivalent and equally acidified bromine solution. The consideration of these oxidation potentials suggested to Bugarsky (*Zeit. Anorg. Chem.*, x., 387) the choice of iodic acid as an oxidiser for the liberation of bromine from mixtures containing a bromide and a chloride.

Bugarsky's method of separating the bromine from such a mixture consists in adding sulphuric acid with a known amount of potassium diiodate, and boiling. The bromine and the iodine which are liberated in the interaction of the free acids, according to the equation $2HIO_2 + 10HBr = 5Br_2 + I_2 + 6H_2O$, escape from the solution and may be collected in the distillate. These free halogens may be made the measure of the bromide taken, or the amount of the bromide may be calculated from the amount of the iodic acid remaining. When the liberated halogens are absorbed in potassium iodide, the amount

* Contributions from the Kent Chemical Laboratory, Yale University, New Haven, Conn., U.S.A.—From the *American Journal of Science*, xxiv., 469.

of free iodine, as determined by titration, proves to be much less than is to be expected from the equation above, and Bugarsky, convinced that the results are much more nearly in accord with the theory when the excess of the iodic acid remaining is made the measure of the reaction, prefers, therefore, to estimate the bromide by determining in an aliquot portion of the boiled solution the iodate which remains, and to determine the chloride in another aliquot portion of the solution by Volhard's process of titration with standard sulphocyanate.

The difference in the results of these two methods of determination Bugarsky attributes to loss of free bromine by the action of steam, in consequence of which hydrobromic acid is formed and oxygen set free, as in the equation $2H_2O + 2Br_2 = 4HBr + O_2$. But Andrews points out that hydrobromic acid thus formed, if returned with the condensed steam to the liquid, must be reoxidised by more iodic acid, with the result that the bromine determination by calculation from the amount of iodic acid remaining will be high rather than low. Andrews' results for bromine were high to the extent of 1 per cent to 1·5 per cent. The differences in experience and view of these investigators have led us to further investigation of the reaction.

Suitable solutions of sodium chloride and potassium bromide* were prepared and standardised gravimetrically by silver precipitation. An iodine solution, approximately N/10, standardised against N/10 arsenite, and N/10 sodium thiosulphate, standardised against the iodine solution, were used. Finally, a solution of potassium iodate (KIO_3) (3·5670 grms. per litre) was prepared, and its iodine value was determined by titrating with the thiosulphate the iodine liberated from 50 cc. portions by the action of potassium iodide in presence of sulphuric acid. To avoid errors of titration due to an indefinite end-point, the gravimetric determination of chlorine was substituted for the Volhard process. Gaseous nitrogen trioxide, liberated from sodium nitrite and washed by nitric acid, was used instead of the sodium nitrite or potassium nitrite used by Bugarsky.

The method of carrying out determinations was as follows:—To 50 cc. of the solution, containing known amounts of sodium chloride and potassium bromide, 50 cc. of the iodide solution of known value and 10 cc. of 20 per cent sulphuric acid were added and the solution was diluted to 200 cc., in a 500 cc. Erlenmeyer flask. A few bits of platinum foil were added, to prevent bumping, and the solution was boiled down to about 80 cc., some thirty minutes being required. After cooling, the solution was transferred to a carefully calibrated 100 cc. flask and made up to the mark.

Half the solution was pipetted into an Erlenmeyer flask fitted with an inverted mushroom trap, through which potassium iodide was added. The liberated iodine was titrated with thiosulphate, and one-sixth of it was taken as the equivalent of the excess iodate in the portion.

The remaining half of the solution was transferred to a beaker, the flask and stopper being carefully rinsed, and an excess of gaseous sulphur dioxide (vaporised from the liquid) was passed in. Gaseous nitrogen trioxide (liberated from sodium nitrite or potassium nitrite by nitric acid, and washed by the same) was passed into the solution to destroy the excess of sulphur dioxide acid and to liberate the iodine. (The nitrogen trioxide prepared in the manner described produced no turbidity in a solution of silver nitrate acidulated with nitric acid). The solution was boiled until free from iodine, and the chlorine of the residual chloride was precipitated by silver nitrate. After standing over night, the silver chloride was filtered off on asbestos in a perforated crucible, dried at gentle heat, and weighed.

The amounts of potassium bromide calculated from the iodate used up, and the amounts of sodium chloride equivalent to the silver chloride weighed, are given in the table, in comparison with the amounts taken of these substances respectively.

KBr taken. Grm.	NaCl taken. Grm.	KBr formed. Grm.	NaCl formed. Grm.	Error in KBr. Grm	Error in NaCl. Grm.	Fina vol. Cc.	
Molecular Ratio of KBr *to* NaCl, 1 : 1.							
0·1984	0·0974	0·2006	0·0995	+0·0022	+0·0021		(*a*)
0·1984	0·0974	0·1981	0·0996	−0·0003	+0·0022		(*a*)
0·1984	0·0974	0·1996	0·1003	+0·0012	+0·0029		(*a*)
0·1984	0·0974	0·1983	0·0996	−0·0001	+0·0022		(*a*)
0·1984	0·0974	0·1939	0·1004	−0·0045	+0·0030	76	
0·1984	0·0974	0·1966	0·1008	−0·0018	+0·0034	74	
0·1984	0·0974	0·1990	0·0998	+0·0006	+0·0024	38	
0·1984	0·0974	0·1945	0·1004	−0·0039	−0·0030	74	
Molecular Ratio of KBr *to* NaCl, 2 : 1.							
0·1984	0·0487	0·1940	0·0517	−0·0044	+0·0030	50	
0·1984	0·0487	0·1904	—	−0·0080	—	65	
0·1984	0·0487	0·1926	0·0519	−0·0058	+0·0032	68	
0·1984	0·0487	0·1965	0·0522	−0·0019	+0·0035	65	
0·1984	0·0487	0·1942	—	−0·0042	—	78	
0·1984	0·0487	0·1945	0·0521	−0·0039	+0·0034	80	
0·1984	0·0487	0·1949	0·0518	−0·0035	+0·0031	65	
0·1984	0·0487	0·1942	0·0526	−0·0042	+0·0039	70	
0·1984	0·0487	0·1959	0·0525	−0·0025	+0·0038	76	
Molecular Ratio of KBr : NaCl, 1 : 2.							
0·1984	0 1948	0·1964	0·1954	−0·0020	+0·0006		(*a*)
0·1984	0·1948	0·1952	0·1990	−0·0032	+0·0042		(*a*)
0·1984	0·1948	0·1967	0·1969	−0·0017	+0·0021		(*a*)
0·1984	0·1948	0·1978	0·1984	−0·0006	+0·0036		(*a*)
0·1984	0·1948	0·1974	0·1980	−0·0010	+0·0032		(*a*)
0·1984	0·1948	0·1983	0·1984	−0·0001	+0·0036		(*a*)
0·1984	0·1948	0·1988	0·1985	+0·0004	+0·0037		(*a*)
0·1984	0·1974	0·1683	0·1028	−0·0001	+0·0054	75	
0·1984	0·1974	0·1960	0·1022	+0·0024	+0·0048	70	

(*a*) The final volume, 50 cc. to 75 cc., was not measured exactly.

In these experiments, made with reagents carefully standardised at the outset and re-standarised in the course of the investigation, the errors are generally large and irregular, independent of the final concentrations within the limits shown, and out of all proportion to any possible chloride contamination of the standard bromide. The fact that the chlorine proves to be invariably high and the bromine generally low, suggests the probability that the iodic acid reaction fails to remove all the bromine in the process of boiling.

Bromine was found in the silver chloride obtained from the combined residues of several determinations by applying the chloroform test to the water extract of the sodium carbonate fusion of these residues, after acidulating with sulphuric acid and adding a drop or two of chlorine water. Furthermore, in a special experiment in which pure potassium bromide was treated according to the procedure outlined, the titration figures of the excess of iodate corresponding to only 0·1945 grm. of potassium bromide out of 0·1984 grm. taken; while, after treatment with sulphur dioxide followed by nitrogen trioxide, and boiling until all iodine had been expelled (as shown by the starch test applied to the cool solution), silver nitrate precipitated from the solution silver bromide equivalent to 0·0036 grm. of potassium bromide. The 0·1945 grm. of the potassium bromide indicated by the determination of the iodate and the 0·0036 grm. equivalent to the silver bromide precipitated after reduction make up 0·1981 grm. of the 0·1984 grm. taken. In this experiment, therefore, the deficiency of bromine and the excess of chlorine noted were plainly due to the retention of bromine, after the iodic acid treatment, in some combination such that the process of reducing the residual iodic acid and expelling the iodine left it in condition to be precipitated as silver bromide, which was counted as silver chloride.

* The "analysed" C. P. article, free from chloride, so far as could be determined by qualitative tests.—*Amer. Jour. Sci.* (3), xl., 289.

The combination of iodine with bromine in this experiment and of iodine with bromine and chlorine in the experiments of the table, would account for the observed deficiencies in bromine and excess in chlorine; and a little consideration shows that the conditions of the process are favourable to the formation of such combinations. Thus free bromine and free iodine, both products of the main reaction, may readily combine to form iodine monobromide, $HIO_3+5HBr=2Br_2+IBr+3H_2O$. Furthermore, Roberts (*Amer. Journ. Sci.* (3), xlviii., 1, 58) has shown that iodic acid, iodine, and aqueous hydrochloric acid react to form iodine monochloride, according to the reaction $HIO_3+2I_2+5HCl=3H_2O+5ICl$, and it may reasonably be expected that in the reaction of iodic acid and hydrobromic acid in presence of free iodine (produced in the main reaction, previously cited) iodine monobromide will be similarly formed, according to the equation $HIO_3+2I_2+5HBr=3H_2O+10IBr$.

When the acidulated solution containing an excess of iodic acid with more or less iodine monochloride, or monobromide, is treated with potassium iodide for the purpose of determining the excess of iodic acid by means of the iodine liberated, $HIO_3+5HI=3H_2O+3I_2$, the iodine compounds of the halogens will contribute to the amount of the free iodine which measures the iodic acid—

$$KI+ICl=KCl+I_2,$$
$$KI+IBr=KBr+I_2,$$

and this increase in free iodine will produce a corresponding deficiency in the bromide, which is estimated from the amount of iodate which has disappeared.

When, on the other hand, the excess of iodate is reduced by sulphur dioxide preparatory to determining the chloride, the iodine monochloride is converted to hydriodic acid and hydrochloric acid, and the iodine monobromide to hydriodic acid and hydrobromic acid. The hydriodic acid is destroyed, and the iodine removed, in the subsequent treatment with nitrogen trioxide; the hydrochloric acid is regularly estimated as silver chloride; but the hydrobromic acid remains to produce silver bromide, which contaminates the sllver chloride and causes an error of excess in the chloride determination.

These hypothetical effects are in precise accordance with the observed phenomena. It is conceivable, and even probable, that chloric acid and bromic acid may appear also as products of the hydrolysis of the halogen compounds in presence of water and iodic acid. Thus the hydrolysis of iodine monobromide may proceed according to the expression—

$$15IBr+5HIO_3+15H_2O = 5HBrO_3+5Br_2+10I_2+15H_2O,$$

and that of iodine monochloride according to the equation—

$$15ICl+3HIO_3+15H_2O = 5HClO_3+10HCl+9I_2+9H_2O.$$

The production of bromic acid by hydrolysis of iodine bromide, with elimination of the free halogens and substitution of bromic acid for an equivalent amount of iodic acid, will tend to reduce the tendency to negative errors in the determination of bromine; but the bromine of the bromic acid will still be capable of contaminating the silver chloride percipitated by silver nitrate after reduction.

The effect of chloric acid substituted for iodic acid will depend upon the conditions of concentration. So far as it may act as an oxidiser in the treatment of potassium iodide, it will tend to produce a positive error in the determination of bromine. So far as it escapes reduction in the treatment of sulphur dioxide and nitrogen trioxide, it will tend to produce an error of deficiency in the determination of chlorine.

The extent to which these various possibilities may influence results will depend upon the conditions of action and possible balancing of errors. The experimental results given above show plainly that under the conditions defined the separation of bromine from chlorine in halogen salts by the action of iodic acid, though based upon a reaction ideal in respect to the relation of the oxidation potentials, is vitiated by secondary effects. These effects may be reasonably attributed to the action of small amounts of iodine monochloride and iodine monobromide formed in the interaction of iodic acid and free iodine with hydrochloric acid and hydrobromic acid, or to the action of chloric acid and bromic acid derived from iodine monochloride or bromine monochloride by hydrolysis.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, March 6th, 1913.

Sir ALFRED KEMPE, Vice-President and Treasurer, in the Chair.

PAPERS were read as follows:—

"*Automatic Method for the Investigation of the Velocity of Transmission of Excitation in Mimosa.*" By PROF. J. C. BOSE.

The research was undertaken to decide the question whether in *Mimosa pudica* stimulus gives rise to a mere passage of hydro-mechanical disturbance or a transmission of true excitation. For this purpose (1) investigation was directed towards devising modes of excitation which are purely physiological and cause no mechanical disturbance; (2) quantitative measurements of the highest accuracy were undertaken to determine in what manner the velocity of transmission is effected by physiological changes; and (3) the question was put to the final test of "physiological block," which is known to arrest excitatory impulse, but could have no effect on the passage of hydro-mechanical disturbance.

In order to eliminate errors of personal observation in the quantitative determination of velocity of transmission, it was necessary to obtain all data from automatic records made by the plant itself. Error introduced by friction of recording surface and other difficulties were overcome by the successful device of the resonant recorder.

In this apparatus the writing lever consists of very light steel-wire accurately tuned to, say, 200 vibrations per second, and kept in resonant vibration. Resistance offered by continuous contact is virtually eliminated by intermittent contacts. The vibrating writer taps a record, intervals between successive dots indicating 0·005 second. The phytogram is thus its own chronogram, the record furnishing accurate time measurements shorter than 0·005 second. Error due to inertia is reduced to a minimum by the lightness of the recording lever, which weighs only 0·04 grm.

For accurate determination of the velocity of transmission, it was necessary to determine also the latent period of the leaf of *Mimosa*.

The researches extended to polar effects of excitatory currents, time difference with ascending and descending currents, comparative sensibility in animal and plant, contrasted effects of anode and cathode, multiple excitation, effect of temperature, and arrest by physiological block.

The results obtained warrant the conclusion that there is transmission of true excitation.

"*Evolution of the Cretaceons Asteroidea.*" By W. K. SPENCER.

"*Preliminary Note on the Fossil Plants of the Mount Potts Beds, New Zealand, collected by Mr. D. G. Lillie. Biologist to Capt. Scott's Antarctic Expedition in the* Terra Nova, *in* 1911.*" By E. A. NEWALL ARBER, Sc.D.

"*Trypanosomes found in the Blood of Wild Animals living in the Sleeping Sickness Area, Nyasaland.*" By Surg.-Gen. Sir D. BRUCE, F.R.S., Majors D. HARVEY and A. E. HAMERTON, Dr. J. B. DAVEY, and Lady BRUCE,

"*Trypanosome Diseases of Domestic Animals in Nyasaland.* II. Trypanosoma capræ (*Kleine*)." By Surg.-Gen. Sir D. Bruce, F.R.S., Majors D. Harvey and A. E. Hamerton, Dr. J. B. Davey, and Lady Bruce.

"*Morphology of various Strains of the Trypanosome causing Disease in Man in Nyasaland. I. The Human Strain.*" By Surg.-Gen. Sir D. Bruce, F.R.S., Majors D. Harvey and A. E. Hamerton, and Lady Bruce.

INSTITUTE OF CHEMISTRY.

Mr. Charles A. Hill, B.Sc., F.I.C., delivered a Lecture on the "*Function and Scope of 'The Chemist' in a Pharmaceutical Works*," on the 12th inst., in the Chemical Lecture Theatre of King's College (by kind permission of the Delegacy of the College). Mr. Otto Hehner, F.I.C., Member of Council of the Institute of Chemistry, was in the Chair.

The Lecturer treated the subject in accordance with the published syllabus of the Lecture, which was illustrated by about twenty lantern slides showing the processes and the plant employed in producing pharmaceutical chemicals and pharmaceutical preparations on the large scale.

Dealing first with the manufacture of chemicals, the lecturer stated that the question of purity is all-important and ought to be settled by a specification; pharmaceutical chemicals had their own peculiar requirements. Traces of impurities so small as to be perfectly negligible for any other technical purpose become objectionable in a pharmaceutical chemical if they consist of toxic substances. The manufacturer must not allow any toxic impurity in such quantity as would be capable, allowing for its physiological action being cumulative, of producing any appreciable physiological effect. Other impurities which may be perfectly negligible from the physiological standpoint may be objectionable to the pharmacist.

The removal of impurities where difficulties arose owing to mass action and the formation of colloidal solutions, the filtration and decolorisation of solutions, and laboratory devices for overcoming difficulties met with on the large scale, were discussed.

The subject of crystallisation was somewhat fully dealt with, the lecturer describing how the same substance was produced in different forms of crystal, as the concentration and quiescence of solutions and the rate of cooling were varied. Specimens of such varieties of the same substance were exhibited.

An ingenious and simple piece of apparatus for obtaining an unlimited supply of hot water in any part of the factory from the cold water and steam mains was illustrated by a diagrammatic sketch on the screen, while a number of photographs were shown of filter-presses, centrifugals, and crystallising tanks actually at work.

The pharmaceutical manufacturing business was stated to offer to the organic chemist an extensive and most attractive field not only in the isolation of alkaloids, glucosides, and other pure active substances from plants, but also in the manufacture of the synthetic organic compounds which enjoy such a large and increasing vogue in the present day practice of medicine. Mr. Hill knew of no valid reason why a combination of capital and enterprise should not in a few years bring about the manufacture in this country of a very large number of substances now supplied to us from the Continent.

In the manufacturing of pharmaceutical preparations the control of raw materials was stated to be far more necessary even than in the case of chemicals, for while it was possible, at an increased cost, to manufacture pure chemicals from materials of low grade, in practically all cases it was quite impossible to produce satisfactory pharmaceutical preparations from drugs of inferior quality.

The standardisation of pharmaceutical preparations and the exact meaning of the word "standardised" in pharmacy was discussed.

The handling of bulks of drug and liquor on the large scale was illustrated, and evaporation, distillation, and drying by means of vacuum plant formed an important feature of the lecture, various designs of apparatus being illustrated both diagrammatically and photographically.

The work which an analytical chemist is called upon to do in a pharmaceutical factory is little different to that he has been trained in, though some of it is of such a specialised type as to be quite new. The duty of the analytical department is to keep a watchful eye on the major portion of the business, and it must to some extent justify its existence by finding fault. Combined with the ordinary routine testing there is a mass of work to be carried out on substances for which there are no standards, and on which the analyst must satisfy himself that they are up to the standard that the prescribing physician has a right to expect. When the question of adulteration is studied it is seen that a considerable amount of experience in pharmaceutical products is necessary before it is possible to identify the adulterant. This is well exemplified in the case of oil of male fern. The first step in getting trustworthy results is to see that the article has been properly sampled. This can only be done by either bulking the whole delivery or testing each package. The routine testing of products which are coming in every week is carried out by such methods as give as accurate results as the time at their disposal will allow.

The deliberate adulteration of various preparations is being carried out with such care that mere routine testing is of little or no avail for detecting it. In this connection is instanced the use of citral derived from lemon-grass oil for sophisticating lemon oil. Thus it is obvious that a considerable knowledge is required of the chemist who has to examine them. Occasionally a perfectly new product is turned out, then the chemist is thrown on his own resources to determine what standard it must satisfy; lastly, the filing of analytical records is of extreme importance.

In connection with the investigation department, there is unlimited scope both for pure research and the investigation of those anomalies which crop up in the course of a day's work. One instance of a valuable by-product was detailed in the production of benzyl cinnamate—an ester valued for its odorous properties—from "spent" balsam of tolu.

Finally, the chemist should keep himself in touch with the purely commercial side of the business, remembering that the successful man in either a pharmaceutical or chemical business is a chemist first and a business man afterwards.

SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS.

Ordinary Meeting, March 5th, 1913.

Mr. Leonard Archbutt, President, in the Chair.

Messrs. John Augustus Goodson, Frederick William Skevington, and John C. White were elected members of the Society.

Certificates were read for the first time in favour of Messrs. Henry Francis Everard Hulton, 15, Oakhill Court, Putney, S.W.; Charles Thomas Kingzett, "Newlands," Weybridge, Surrey, and "Maplin," Frinton-on-Sea, Essex; and Alfred James Parker, 1, Bulwer Street, Herne Bay, Auckland, New Zealand.

Certificates were read for the second time in favour of Messrs. Arthur Cecil Bescoby, Thomas Walter Firth Clark, Frank Edward Day, and James Fowler Tocher.

The following papers were read and discussed:—

"*Accurate Determination of Carbon Dioxide in Carbonates.*" By Frank Sturdy Sinnatt.

The method described consists in collecting, in an evacuated vessel, the carbon dioxide evolved when

carbonates are decomposed by means of acids. In order to render this a process convenient to carry out, an apparatus described by Sinnatt (*Analyst*, June, 1912) is used. The carbon dioxide is determined subsequently by applying Pettenkofer's process to the resulting gaseous mixture.

"*Bacterial Testing of Disinfectants.*" (A Practical Criticism). By C. T. Kingzett and R. C. Woodcock.

The authors have determined the bactericidal coefficients of some seventy-seven substances by the Rideal-Walker test, and conclude—(1) That the value of the Rideal-Walker test is strictly confined to the so-called coal-tar class of disinfectants; and (2) that the intensity of germicidal action affords no measure of the value of disinfectants as practically applied.

"*A Quick and Improved Method for the Estimation of Boric Acid in Milk and Cream.*" By Frederic W. Richardson and William Keighley Walton.

The authors employ copper sulphate and heat for the precipitation of the curd with or without subsequent addition of zinc powder to remove the copper. The filtrate after neutralisation to phenolphthalein is mixed with glycerin, and a special factor is used in the calculation.

"*Simple All-glass Extraction Apparatus.*" By Clayton Beadle and Henry P. Stevens.

The apparatus consists of an Erlenmeyer flask with wide elongated neck. The extraction tube with syphon is suspended from three or four projections at the bottom of the neck, and the condenser tube is suspended in the neck of the flask, which should be 4 or 5 inches long and about 1½ inches wide.

THE BIOCHEMICAL SOCIETY.

The Annual General Meeting of the Biochemical Society was held in the Chemical Department of the London Hospital Medical College on Thursday, March 13, 1913, at 5 p.m. Mr. Hugh Candy in the chair.

The following communications were given :—

"*The Old and a New Test for Acetoacetic Acid.*" By W. H. Hurtley.

"*A Sensitive Modification of Gmelin's Test for Bile Pigment in Urine.*" By J. H. Ryffel.

"*The Combination of Amino Acids with Neutral Salts.*" By W. M. Bayliss.

"*The Separation of Cystine and Tyrosine.*" By R. H. A. Plimmer.

Messrs. E. C. Grey, J. Henderson Smith, W. Ray, and C. G. L. Wolf were elected Members of the Society.

THE ALCHEMICAL SOCIETY.

The Third General Meeting of this Society was held on Friday, March 14th, at 8 p.m., at the International Club, Regent Street, S.W. The Chair was occupied by the Acting President, Mr. H. Stanley Redgrove, B.Sc. (Lond.), F.C.S., and a paper dealing with the "*Interpretation of Alchemy in Relation to Modern Scientific Thought*," by Messrs. Leonard F. Pembroke and Sijil Abdul-Ali, was read by the latter.

The Lecturer pointed out that the alchemists in general appeared to have adopted the Hermetic method of reasoning from universal to particular judgments, although there were sporadic indications in the literature of a quite scientific and rational empiricism. The fundamental concepts of their philosophy were, he said, (i.) A "first matter" of "Hyle," containing implicitly the four elements which were subsequently to issue in manifestation; (ii.) four elements (viz., earth, water, air, and fire) which by mutual combination produced the three principles (viz., sulphur, mercury, and salt), whose varying combinations gave rise to the different properties of bodies; (iii.) a certain divine Spirit or essence, called "The Soul of the World," which was imminent in all created things; and (iv.) a mediate Spirit, called "The Spirit of the World," by which the soul acted upon and was bound to its body (*i.e.*, matter).

The lecturer compared and contrasted these concepts in a most interesting manner with modern scientific theories concerning :—(i.) A possible dual protyle, or first matter; (ii.) the solid, liquid, gaseous, and incandescent-gaseous states of matter; (iii.) energy; and (iv.) the ether of space. The full text of the lecture and an abstract of the discussion which followed will be published in the March number of the *Journal of the Alchemical Society*.

NOTICES OF BOOKS.

General Index to the Chemical News (Vols. I. to C.). London : *Chemical News* Office. (Price, £2).

It cannot be doubted that there will be differences of opinion as to the merits of this Index, nor hoped that users of it will have no adverse criticisms to offer, but the methods adopted in it are believed to be those which in the main will prove to be the most convenient and time-saving. The Index includes both subjects and authors. Under the names of the latter all contributions they have made to the Chemical News are enumerated, as well as any personal notes and reviews of their publications, or abstracts of their papers, which may have appeared in its pages. When an author has published work in collaboration with another, as well as in his own name only, it is given under separate headings. Again, a large subject such as "Acid" is sub-divided as far as possible. The individual acids are given separately, as well as the word used in its general sense, while "Acids" also constitutes another heading. "Alcohol" and "Alcohols," "Water" and "Waters" and metals and their salts are similarly treated. A complete list of Book Reviews and Notices is given under "Book," and every notice also appears under the name of the author of the book. In indexing articles and papers the spelling and nomenclature originally used by the authors are exactly followed; hence, "sumac" and "sumach" will be found, and "radicle" and "radical." Where cross references have been thought to be necessary they have been inserted, and every effort has been made to enable readers of the Chemical News to look up quickly and easily any subjects which have appeared in its pages, however fragmentary and incomplete their knowledge or recollections of them may be.

Achievements of Chemical Science. By James C. Philip. M.A., D.Sc.(Aberdeen), Ph.D.(Göttingen). London ; Macmillan and Co., Ltd. 1913.

Teachers of chemistry have every reason to be grateful to the author of this little book, which is eminently readable and will undoubtedly stimulate interest in the science. It may be put into the hands of boys and girls in the middle and upper classes of schools, who will find that it is interesting and clear, and is not in any way childish or trivial. Teachers will do well to refer to it for suggestions as to methods of dealing with descriptive chemistry, which is apt to become too heavily loaded with facts and details only too easy to forget, and the general public interested in science will find that it is not by any means beneath their notice. Stress is laid upon the history of scientific discoveries, and accounts are given of the lives of some of the great investigators. The text is quite up-to-date, and includes allusions to synthetic rubber, the ultramicroscope, the Brownian movement, &c., while present day problems are put vividly before the reader.

A History of Chemistry. By the late James Campbell Brown, D.Sc.(Lond.), LL.D.(Abdn.) London: J. and A. Churchill. 1913.

The text of this book has been prepared from manuscript notes of lectures on the History of Chemistry delivered at Liverpool University by the late Dr. Campbell Brown, of whom a short biographical notice is included. The editor was obliged to divide the text into chapters, which did not exactly coincide with the lectures, but for the main division of the history into five periods the lecturer is responsible. Of these five periods—the Prehistoric, Alchemical, Iatrochemical, Phlogiston, and Quantitative Periods—the earlier ones are treated in comparatively greater detail, which may be regarded as an advantage from some points of view, on account of the greater inaccessibility of sources of information. The author appears to have made a special study of the beginnings of the science, and his accounts of early theories and conceptions and his reproductions of primitive apparatus are of the greatest interest. The dependence of the history of chemistry upon the general history of the nations is skilfully shown, and the student will gain a good deal of general historical information from the book. In some matters of detail it would have been worth while to bring the text up-to-date and make a few corrections; for example, it contains the statement that radium has not been isolated, and the elements "praseodidymium" and "neodidymium" are mentioned as constituents of didymium.

The Principles of Applied Electrochemistry. By A. J. Allmand, D.Sc. London: Edward Arnold. 1912.

The electrochemistry of aqueous solutions is fully treated in the first part of this book, which also includes chapters on the electrolysis of fused melts, electrothermics, and the discharge of electricity through gases. A feature of the text is the thoroughness with which main principles are emphasised, and while no more theory is introduced than is absolutely necessary, the author has been very careful not to under-estimate this amount, and the student or practical man who has followed and thoroughly assimilated the first part should have no difficulty in dealing with Part II., in which the various technical processes employed are described and discussed. No statistics or details of costs are given, but, on the other hand, the book contains thoroughly scientific accounts of processes which are actually in use either in Europe or America. In rare cases methods which have not proved successful in practice are included, but this is usually the case when there is something to be learnt from their failure.

The Metals in Antiquity. By William Gowland, Assoc.R.S.M., F.R.S., F.S.A. London: Royal Anthropological Institute of Great Britain and Ireland. 1912.

This reprint from the *Journal of the Royal Anthropological Institute* contains the Huxley Memorial Lecture for 1912. The lecture will be found interesting by chemists as well as by anthropologists. The lecturer described the discovery of the process of extracting metals from their ores, which he believes to have been made accidentally, owing to the use of a lump of ore as a stone surrounding a camp fire, which was in fact the first metallurgical furnace. He points out that the "hole in the ground" furnace, which developed from it, was in 1872 still in use in Japan, where until quite recently methods for obtaining all the useful metals—copper, lead, iron, and tin—differed only very slightly from those used by the men of the stone age. After a general discussion the individual metals are considered in detail, and the paper is enriched with many interesting photographs and diagrams.

Year Book of the Indian Guild of Science and Technology, 1912. Letchworth: The Letchworth Printers, Ltd.

This year book of the recently founded Indian Guild of Science and Technology contains a report of the annual meeting of the Guild, held at Birmingham. At this meeting Mr. J. R. R. Wilson, late Chief Inspector of Mines for India, read a very interesting paper on coal-mining in India, in which he gave an admirable survey of the present state of the industry, and discussed some of its more serious problems. Other papers read before meetings of the various local sections are also reproduced in the year book, and abstracts of articles published in the scientific journals by members of the Guild are also included.

Grundzüge der Pharmazeutischen Chemie. ("Outlines of Pharmaceutical Chemistry"). By Dr. Heinrich Beckurts. Vol. I. Leipzig: S. Hirzel. 1912. (10 M.).

In this book inorganic chemistry is treated in such a way as to lay special stress upon those facts which are of the greatest importance to pharmaceutical chemists. A fairly detailed account is given of all the common elements; the history of their discovery is outlined, and their applications, preparation, and properties, as well as those of their compounds, are discussed. In addition methods of testing drugs are included, and also data relating to the properties of special preparations and drugs, with copious references to the German Pharmacopœia.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clvi., No. 1, January 6, 1913.

Photolysis of Ethyl Alcohol and Aldehyde and Acetic Acid.—Daniel Berthelot and Henry Gaudechon.—When ethyl aldehyde is subjected to ultra-violet rays various reactions occur:—(i.) Carbon monoxide and methane are formed; (ii.) polymerisation occurs, and liberation of condensed gaseous hydrocarbons such as ethane; (iii.) formation of resinous products insoluble in water; (iv.) acidification by internal combustion and transformation of the aldehyde into pure acetic acid. The first reaction occurs in the ultra-violet, where $\lambda > 0{\cdot}3\ \mu$, and the three others in the mean and extreme ultra-violet. Ethyl alcohol and acetic acid do not undergo photolysis under the action of light of greater wave-length than $0{\cdot}3\ \mu$.

Basicity of Tungsto-acids.—H. Copaux.—Silicotungstic acid is a strong acid which rapidly attains a limiting conductivity, equal to four times that of hydrochloric acid. Even when strongly diluted it is a tetrabasic acid, practically insensible to hydrolysis. Its isomer (probably stereochemical) tungstosilicic acid and the isomorphous silicomolybdic acid behave in the same way. The conductivity of borotungstic acid is equal to five times that of hydrochloric acid. It is thus pentabasic. Metatungstic acid is hexabasic, but it is a weaker acid than the preceding and undergoes hydrolysis at great dilutions. Phosphotungstic acid is hydrolysed, and from the composition of its salts appears to be tribasic.

2-2-Dimethylcycloheptanone.—P. J. Tarbouriech.—When isopropylcyclohexylpinacone is dehydrated two isomeric ketones, $C_9H_{16}O$, are formed. The first of these is 1-methyl-1-ethanoylcyclohexane, and the second the author has now shown to be 2-2-dimethylcycloheptanone. Thus a chain containing seven atoms of carbon is obtained from a hexatomic nucleus. The oxidation of this ketone shows that the group CO in pinacolic ketones is peculiarly resistant to oxidation.

No. 2, January 13, 1913.

Occlusion of Products of Radium.—M. Costanzo.—Palladium in thin layers occludes the disintegration products of radium about as well as rubber. In occlusion phenomena the thickness of the active layers seems to have some slight influence which is appreciable but has not yet been exactly defined. For thick layers the activity observed when the substance is withdrawn from the sphere of activation is greater with palladium than with rubber.

Alloys of Aluminium with Vanadium. — Nicolas Czako.—By the aluminothermic method the author has obtained a series of alloys of aluminium and vanadium containing from 30 to 80 per cent of vanadium. By fusion with aluminium alloys containing less than 30 per cent can be obtained. Up to 10 per cent of vanadium the alloys are malleable; from 20—25 per cent they can be pulverised. Up to 53 per cent they were full of cavities, which made it difficult to obtain a polished surface. The hardness of the alloys increases with the proportion of vanadium up to the compound Al_3V, and thence up to 53 per cent of vanadium. The hardness of the last is between 6 and 7. From 60—80 per cent they are less hard and are free from cavities.

Analysis of Mixtures of Hydrogen and Gaseous Hydrocarbons. — P. Lebeau and A. Damiens. — The eudiometric method of analysing gaseous mixtures of hydrocarbons is unsatisfactory when more than two hydrocarbons are present. The authors have found that the distillation of the gases after liquefaction makes it possible to fractionate them into portions of definite known composition, for which eudiometric analysis can be employed.

Fixation of Alkaline Bisulphites by the Salts and Ether-salts of Acetylenic Acids.—Ed. Lasausse.—It is possible to fix one or two molecules of alkaline bisulphite on the salts or ether-salts of acetylenic acids of general formula $R—C\equiv C—CO_2H$. The triple bond disappears and the alkaline salt of a monosulphonic acid with an ethylenic band, or the alkaline salt of a saturated disulphonic acid, is formed. Thus sodium sulphite reacts with phenyl-propiolic acid to give disodium β-sulphocinnamate—

$$C_6H_5—C\equiv C—CO_2H + SO_3Na_2 = C_6H_5—C(SO_3Na)=CH—CO_2Na.$$

Also sodium sulphite reacts with methyl phenylpropiolate to give the cinnamate of methyl-monosulphonate of sodium and the phenylpropionate of methyl-disulphonate of sodium. Methyl amylpropiolate can fix two molecules of sodium sulphite, giving the saturated disulphonic derivative.

Bulletin de la Société Chimique de France.
Vol. xiii.-xiv., No. 2, 1913.

Action of Hydrogen Peroxide on Alkaline Solutions of Lead Oxide.—V. Zotier.—When H_2O_2 acts on lead oxide PbO_2 is formed. As the quantity of H_2O_2 increases the quantities of PbO_2 increase up to a certain limit and then remain constant. The limit is reached when equimolecular quantities of PbO and H_2O_2 are reacting. The equation is $5PbO + 5H_2O_2 = 5H_2O + 2PbO_2 + 3PbO + 3O$. The quantity of PbO_2 formed diminishes as the temperature is raised. Dilution has only a very slight effect on the reaction. The quantity of PbO_2 formed diminishes as the ratio NaOH : PbO is increased.

Determination of Copper in Jam.—E. Tassilly.—When solutions of copper ferrocyanide are studied spectrophotometrically it is found that the absorption is proportional to the amount of copper in the solution, and a method of determining copper in jam may be based upon this fact. The jam is dried, slightly charred, and digested with sulphuric acid. The copper is separated from iron by precipitating with sodium hyposulphite, filtered off, and ignited. The residue is taken up with sulphuric acid and a little HNO_3, the two acids are evaporated off, and the residue is dissolved in 100 cc. of water. The solution is then examined with a spectrophotometer, after the addition of a solution of potassium ferrocyanide. Comparison with solutions containing a known amount of copper gives the percentage of copper present in the jam.

Determination of Nitric Oxide.—MM. Koehler and Marqueyrol.—Nitric oxide in gaseous mixtures containing N_2O, NO, N_2, CO_2, CO can be determined by converting it into N_2O_3 and absorbing the latter by monoethylaniline. About 80 cc. of the gas to be analysed are passed into a graduated vessel over mercury, and 0·6 cc. of monoethylaniline is added. Then oxygen is bubbled in, till about 5 cc. are present in excess. The residual gas is measured, 0·2 cc. of caustic potash (1 : 1) is added, and after it has been separated off a fresh reading is taken. The diminution in volume represents the volume of CO_2. Pyrogallic acid is finally added to absorb the oxygen.

Apparatus for Determinations by Electrolysis.—F. Chancel.—A convenient apparatus for carrying out electrolytic determinations can be made out of a Jena glass tube of about 30 mm. diameter and 125 mm. in length. One end is closed, and through it a wire of platinised iridium passes; this acts as the anode. The cathode is a cylinder of platinum gauze suspended by a platinum wire. The liquid to be electrolysed is put in the tube, which is then closed with a watch-glass.

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xlv., No. 17, 1912.

Formation of Nitric Oxide in High Tension Arc.—Franz Fischer and Emil Hene.—The formation of nitric oxide in the high tension arc is due to the activation of the oxygen and not to that of the nitrogen. The best yield of nitric oxide is obtained if sparked oxygen is allowed to act upon unsparked nitrogen, and the worst yield is obtained when the nitrogen is sparked and blown into pure oxygen. If the air proceeding from the high tension arc is passed into oxygen, considerably more nitric oxide is obtained than if it is mixed with air or nitrogen and thus cooled. Thus it seems not impossible that better yields of nitric oxide would be obtained in practice if oxygen only and not air was led through the high tension flame, magnetite electrodes being used, and the oxygen was then rapidly mixed with nitrogen and cooled. Thus the air would be first fractionated by Linde's method, the oxygen then exposed to the high tension flame, and finally mixed with the nitrogen.

MISCELLANEOUS.

Determination of Alkaloids in Cinchona. — L. Ployart and C. Vallée.—To determine the alkaloids in cinchona the best method is one which is adapted from that of the Belgian Pharmacopœia and Yvon's method. The dried powder is left in contact with chloroform and ammonia. The chloroform is distilled off, and the residue is dissolved in alcohol and ether. Hydrochloric acid is added, the ether is driven off on the water-bath, and the solution is finally precipitated with silicotungstic acid.—*Journal de Pharmacie et de Chimie*, [7], vol. vii., p. 118.

Chemical Laboratory Fresenius, Wiesbaden, Germany. — During the Winter Term, 1912-13, the Chemical Laboratory Fresenius was attended by thirty-four students, including four ladies. Of these twenty-four were from Germany, three from Luxemburg, two from Russia, one from France, one from Holland, one from Spain, and one from Brazil. There were two assistants in the Instruction Laboratory, and twenty-nine in the private laboratories (Versuchsstationen). To the teaching staff of the institution belong the Directors, Geh. Regierungsrat Prof. Dr. H. Fresenius, Prof. Dr. W. Fresenius, and also Dr. R. Fresenius, Dr. L. Grünhut, and O. Schmidt (architect). The next Summer Term begins on April 24. During the Winter Term, 1912-13, besides the scientific researches, a great number of analyses were undertaken in the different departments of the Laboratory (Versuchsstationen) on behalf of trade, manufacture, mining, agriculture, hygiene, justice, and government.

THE CHEMICAL NEWS.

Vol. CVII., No. 2783.

THE LIFE NUTRIENT IN FOODS.

By ERNEST L BRIGGS.

(Concluded from p. 135).

Rutherford's next experiments were for the purpose of determining what relation Trophogen bore to the so-called nutrients Fats, Proteins, Carbohydrates, and Ash. Food from which every particle of Trophogen had been removed formed the basis of these experiments. Kittens fed on it starved to death as quickly as if they had not been fed at all. As fat is contained in Lipoid, Rutherford experimented to determine if fat could possibly be the vital principle of food. So he added fats, such as Palmitin, Olein, and Stearin. The addition was not of the slightest value, and the kittens starved to death. Thus he proved that Fat, which we have been taught to regard as one of the important nutritive principles of food, contains no particle of nutriment in itself. Next Rutherford set about to determine the status of the dietist's Protein. Trophogen was extracted from many different Protein foods, so-called, and the kittens were fed on the residual. They died as in the former case. Thus Protein was proved to possess no nutriment. In a like manner he experimented with Carbohydrates, the result being the same. Hence neither Fats, Proteins, nor Carbohydrates contained any alimental substance outside of the Trophogen that was in them. As Mr. McCann believed Ash to be the life-sustaining constituent of food, Rutherford made tests to determine its food value. To the residual mass he added the different organic salts—calcium, iron, magnesium, phosphorus, and others—and still the kittens could not survive. But after the Trophogen had been returned to the foods it proved thoroughly life-sustaining and the kittens thrived on it. The proof was positive, therefore, that Trophogen, and Trophogen alone, was the nutritive element in foods, that no food or food substance would sustain life without it.

In the experiments of both Rutherford and Stepp it was found that the addition of lecithin or cholesterin to the devitalised food had no effect in sustaining or prolonging life.

Perhaps the most remarkable of the incidental experiments was that proving butter-fat to contain no food value. Both Rutherford and Stepp added butter-fat to the residuum and found it to be valueless in keeping the animals alive. The milk plasma, however, was found to be very nutritive. An extract from dried butter-milk kept Rutherford's kittens alive and well. Boiled milk was found to be exceedingly low in its Trophogen contents. Kittens grew emaciated when fed on it. And the evaporated extract from boiled milk was so very low in Trophogen that when added to the basic residuum it was not of sufficient nutritive value to sustain life.

How revolutionary these results appear! How ridiculous they make the advice of our experts and health authorities to "boil the milk," "see that the milk is pasteurised," and that the butter contains specified quantities of butter-fat. Boiled and pasteurised milk are nearly the same. If Rutherford is right the milk plasma alone is the aliment of milk and milk products. This it is that makes cheese wholesome, and causes butter-milk and fresh sweet milk to be so healthful and nutritious.

But while the new tenets may puzzle us in these regards they throw much light on matters that have perplexed both the scientist and the layman. They explain why country children keep healthful on clabbor and butter-milk. They explain better than anything else why food adulterations are harmful. They are so simply because they rob the system of the nutriment it needs, for chemical preservatives are shown to be destructive of Trophogen, especially the vital element, Biogen. The harm is shown to lie not so much in the presence of the chemical as we have supposed, but in the fact that the chemical removes much of the Biogen, the real life of the food. In the great bleached flour war, resulting in the prohibition by the United States Government of the bleaching process, the strongest argument of the millers was that it was impossible for any of the bleaching chemicals—nitrates and nitrites—to remain in the finished flour. The Government was unable to disprove this assertion, and the bleaching was prohibited mainly on the grounds that the bleached flour was less nutritious than the whole-wheat flour, and that through the bleaching process millers were enabled to use any kind of inferior wheat which made a finished product that could not be detected from the flour of the purest and best wheat. The discovery of Trophogen shows that it was the removal of a part of this constituent that was the real cause of bleached flour's harmfulness. The same is true of polished rice, and of fruits, syrups, and vegetable products treated with sulphites and ethers as bleaching and preserving agents. Let it be impressed on the mind that the chemicals do not destroy or even impair the Trophogen that remains in the food, but evaporate much of it from the food by something of the same manner that it was extracted in the kitten experiments made by Rutherford. Wherever Trophogen exists it is wholesome. It is its absence that impairs the food. As long as it remains in the food it is well nigh indestructible. The danger lies in taking it out of the food.

But the retention of Trophogen in garnered foods does have a strong tendency to produce decay. The most effective way of preserving a product is to remove as much of the Trophogen as possible. That is why the manufacturer unknowingly has been at enmity with Trophogen. It is the life-principle of living organisms that undergo changes as in germs. Therefore, all chemical-preserving processes have unknowingly been for the purpose of extracting the Trophogen so as to make the food keep. This seems to say that the more indestructible a food is made the more harmful it is, and that is about the fact in the case. Under the old processes of milling, flour and meal became musty in a short time and soon spoiled. Now it will keep almost indefinitely, and it is substanceless just in proportion to its keeping power. The discovery shows that many of the most healthful foods are those that would decay most rapidly without the aid of a preserving agent, and this too is borne out by every-day observations. It explains why fresh luscious fruits are very healthful, and shows that the chemical processes of preserving them are harmful just to the extent that they are preserving. It explains why milk, fish, and eggs are more healthful the fresher they are. Salt, sugar, spices, and such simple preservatives, however, do not rob the foods of Trophogen, but merely arrest its tendency to decompose, or rather to protect it from the agents of decomposition without extracting the nutrients. Besides they in themselves contain considerable Trophogen. This is not true of other preservatives. However, Trophology teaches us that no foods are so healthful as those in the fresh state, placed before us as nature intended, and without the intervention of any preserving agent whatsoever.

Rutherford's experiments prove conclusively that Trophogen is an essential constituent of all vegetable and animal tissue. It is not the nuclei of protoplasm, as some may venture to assert, but is an even more subtle substance contained in the outer wall of protoplasmic cells. While present in all cells, both animal and vegetable, the animal Trophogen is derived exclusively from vegetable food. The vegetable kingdom is its sole manufacturer or compiler.

As the bee collects honey from the flowers, so the vegetable kingdom gathers Trophogen from the light and warmth of the sun, from the dew of the night, and the

beams of the moon, from the rain, and from the mineral compounds of the earth and air– from all these to a considerable extent, but mainly from an asomatous and extramundane source the human mind cannot comprehend.

Trophogen exists in the body tissue of the human being just as in the food from which it is obtained, and seems to undergo but little change. The proportion of Biogen and Sarcogen varies in different cells, the Biogen being more plentiful in the nerve cells and in other tissue that manifests "vital properties." The strange feature is that it should retain its vitality and life-giving principles in spite of the action of fire, and the processes of grinding and pressing to which food is subjected in the course of preparation. However, it seems wonderfully indestructible, and can only be taken from the food by the chemical process of extraction. It cannot be killed in the food, it seems, but it can be taken out of the food. As long as food is food the Trophogen is there. When its food value is destroyed, as in burning or decomposition, the Trophogen is destroyed. The relation between animal and vegetable Trophogen is best explained by Rutherford himself. He says :—

"While the vegetable kingdom, being the sole manufacturer of Trophogen, thus becomes the origin of all life as we know it, it does not follow that foods are always best adapted for human sustenance in the vegetable form. The flesh of the animal that feeds on vegetable food seems to be ideally adapted to human sustenance as our digestive organism is at present constituted. The Trophogen food which the herbivorous animal has obtained from the vegetable kingdom is supplied to us in animal flesh often in more edible and concentrated form, and the food is thus rendered more digestible, more assimilable. The herbivorous animal seems to be Nature's mill, which, after receiving from the vegetable kingdom the nutriment necessary for our sustenance, grinds it up, discards the chaff, and otherwise prepares it for us in a more palatable and nutritious form. That is to say, the animal has performed much of the manipulation our own system would have to perform if we should eat the vegetable food direct.

"But after the flesh of the herbivorous animal has been eaten by another animal, the Trophogen undergoes transformation, which makes it less suitable for food. From this reason, perhaps, we seem to have a natural repugnance for the flesh of carnivorous animals. The flesh of the cat and dog, while life-sustaining, is not prized as food. It is not difficult, however, to change any animal from a carnivorous to a herbivorous diet, and *vice versâ*. And in countries where canine flesh is eaten it is customary to feed the dogs on a vegetable diet before slaughter. Most of the important food animals are herbivorous. The Trophogen does not seem to deteriorate so much in passing through successive stages of the lower animal forms. Chickens and other edible fowls eat insects and such small invertebrates, but their food is mainly vegetable; while the hawk, the owl, the eagle, and similar birds of prey are not generally eaten by man. Fishes, on the other hand, never eat what is called flesh, nevertheless they subsist almost entirely on animal food, eating each other and all manner of small invertebrates. But fish is not defined as flesh, and there are peculiarities about its nutritive composition that have not been explained. Suffice it to say that in fish, as well as in all other forms of food products, the nutritive element is Trophogen, and in the sea its source is found in the sea-weed, which directly or indirectly sustain all the life of the ocean. The insect, the worm, and other such small invertebrates are very closely associated with vegetable life, and it is probable that in them and in fishes the Trophogen retains its vegetable character better than in other forms of animal life. The higher the form of animal life, it seems, the greater the extent of the Trophogen transformation. And withal, the rule holds good in the main, that Trophogen which has passed through more than one flesh form is not well adapted to human nourishment, and instinctively we have a distaste for flesh foods of this kind."

It might be said, therefore, that the herbivorous animal is Nature's storehouse and refinery of Trophogen, and the carnivorous animal is the feeder from this storehouse. Cannibalism might now have its meaning revised to comprehend the eating of the flesh of one carnivorous animal by another, for this in truth is a thing abhorrent to nature.

Mankind seems to have an instinctive comprehension, without exactly knowing why, that the herbivorous animal is the medium through which we obtain a large amount of our food supply from the vegetable kingdom. Thus when we speak of any peoples being large consumers of a certain cereal, we always imply that the cereal is consumed through the food animals as well as by the people direct. Cattle and hogs in America, for instance, often are referred to as "corn on the hoof." The consumption of corn in this wise is second only to that of rice, and its food value is greatly enhanced by being converted into flesh.

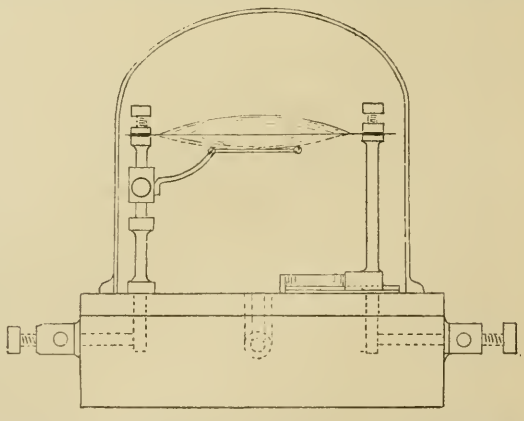
As Newton overturned old traditions by his law of gravitation, as radio-activity upset all previous calculations as to the make-up of matter and the age of the earth, the geological periods, and the sources of heat and changes of the seasons, so has the discovery of Trophogen set at naught all our former reckonings regarding food values.

THE APOPHOROMETER.*

By J. JOLY, F.R.S., Iveagh Geological Laboratory.†

WHEN recently looking over some of my records of experimental work dating back to 1885-86, I came across a suggestion of an apparatus which, as I now believe, deserves to be disinterred and suitably named. The name at the head of this paper means a measurer of sublimates. The instrument is, in fact, one for enabling sublimates obtained from substances at high temperatures to be collected in their entirety and weighed on the chemical balance for purposes of chemical analysis, identification, or research.

The apophorometer is a very simple instrument. A ribbon of thin platinum, about 6 cm. in length, and 4 or 5 mm. in width, is stretched between two forceps which are



provided with binding-screws so that a current can be sent through the ribbon, raising its temperature to any desired degree up to the melting-point of platinum. One of the forceps is movable, and is so acted on by a light spring that the ribbon is kept stretched. The substance to be volatilised is placed in the form of powder upon the ribbon or hob. Beneath the ribbon a watch-glass is held in

* Ἀποφορά (ἀποφέρω), a sublimate. I owe the suggestion of this name to Prof. Henry H. Dixon, F.R.S.

† From the *Philosophical Magazine* for February, 1913.

position by a support which can be raised or lowered or rotated to one side. When this watch-glass is in contact with the ribbon a second watch-glass is placed on the lower one. The ribbon is thus enclosed between the glasses for nearly its entire length. Over all a receiver fits enabling an indifferent gas to be introduced around the heated substance or a vacuum to be established.

The procedure is as follows :—The lower watch-glass is raised till it is in contact with the ribbon. From 5 to 30 mgrms. of the substance are distributed over the ribbon so as to extend nearly over its entire length. The upper glass is then laid on. All is now ready for the experiment. In some cases it is desirable to weigh the platinum ribbon before placing it in position. And, again, in some cases it is advisable to make a preliminary experiment on a portion (not weighed) of the powder in order to observe the behaviour of the substance.

A current is now passed through the ribbon and gradually increased. It may be that more than one sublimate is obtainable from the substance by careful regulation of the temperature; or it may be that only the one is to be expected, and the residue being non-volatile very great care in raising the temperature is unnecessary. When the sublimate is coming off freely the high temperature is maintained unaltered for from ten to fifteen minutes, or until the sublimation is seen to be completed. The current is then cut off, and the glasses let cool; but while still considerably above air temperature the upper glass is lifted off, the lower one let down and removed, and both glasses are clipped together for weighing. This is important, as some sublimates are hygroscopic. It is well to use watch-glasses which are ground to meet accurately.

I have assumed that the presence of oxygen is not injurious. In many cases it is not. If it is, the receiver must be taken into use and the air excluded.

If there is any uncertainty as to the completion of the process, a second pair of watch-glasses should be placed around the ribbon, and the current again turned on. We can thus make sure that the volatile constituent has been completely removed.

The whole process is one of ease and simplicity. In most cases the nature of the sublimate is anticipated, and in others its character enables it to be determined; and, of course, chemical tests may be applied to it after its weight has been ascertained. Knowing the nature of the sublimate, the combined oxygen may be calculated out.

The weight of residue left upon the ribbon is in some instances of importance. But it is necessary to bear in mind that the residual element may be oxidised in those cases where access of oxygen has been permitted. It will sometimes be found that from this cause the residue may actually weigh more than the original sample of the substance.

Certain substances may alloy with the platinum, and, owing to the extreme thinness of these wide ribbons, cause it to fuse. These may be dealt with either on heavier platinum ribbon or on carbon. Moulded strips of carbon would, doubtless, be obtainable. In point of temperature-range carbon has also advantages, but this is of minor importance, for there are few sublimates not obtainable by the use of platinum. It should be remembered that ordinary carbon may contain volatile impurities. If we desire to deal with very high temperatures, the watch-glasses should be of transparent vitreous silica.

I will now quote a few recent results as illustrating the uses of the apophorometer.

Clausthalite, PbSe.—Pb, 72·4; Se, 27·6. Weight taken, 21·5 mgrms.

1. The substance fused at a very low red heat, and a brick-red sublimate collected (Se). Weight of sublimate, 6·2 mgrms.

2. The residue on the ribbon presented the appearance of litharge. A re-heating at former temperature gave no further sublimate. But when the temperature was brought to a full red a copious white sublimate was formed. Weight, 12·4 mgrms.

Some litharge still adhering to the ribbon, this was weighed and found to be 6·6 mgrms.

Taking the sublimate as PbO and the residue as approximating to the same composition, we have Pb = 17·6 and Se = 6·2. On the formula the weights should be Pb = 15·6, Se = 5·9. This was the first gravimetric experiment on sublimates which I made.

Proustite, Ag_3AsS_3.—Ag, 65·4; As, 15·2; S, 19·4. Weight taken, 11·3 mgrms.

1. At a temperature below visible red a rapidly formed white sublimate collected (As_4O_6). Weight, 2·1 mgrms.

2. No further sublimate was obtained at temperature of (1). The residue was a blackish slag suggesting Ag_2S. Raised to a dull red the residue slowly whitened and took on a metallic lustre (Ag). A very small trace of whitish sublimate also appeared. On weighing the ribbon the silver was found to amount to 8·3 mgrms.

Taking the white sublimate as As_4O_6 we have As = 1·5. Also Ag = 8·3. By difference 1·5 mgrms. of S have passed off as SO_2. On the formula the weights should be Ag = 7·4, As = 1·7, S = 2·2. In nature considerable departures from the theoretic proportions occur in substances such as the above.

Niccolite, NiAs.—Ni, 43·9; As, 56·1. Weight taken, 26·5 mgrms.

At a sub-red heat a white sublimate of As_4O_6 was formed. Weight, 16·7 mgrms. This contains 12·7 mgrms. of As, and, by difference, Ni = 13·8. On the formula As = 14·8 and Ni = 11·7.

In this experiment the precaution of re-heating was not at first carried out. The result shows a deficiency of As, and it was afterwards found that more sublimate was obtainable from the residue. A fresh experiment was made :—

Niccolite, as above. Weight taken, 30 mgrms.

1. Raised to dull red; weight of sublimate obtained, 22·1 mgrms.

2. No further sublimate formed.

From this As = 16·7 mgrms., and, by difference, Ni = 13·3 mgrms. From the formula the quantities should be As = 16·8, Ni = 13·2.

Sylvanite (Au, Ag), Te_2.—Ag, 13·4; Au, 24·5; Te, 62·1. Weight taken, 9·2 mgrms.

1. At a sub-red heat a grey-black sublimate formed; weight, 1·4 mgrms. The temperature was now raised to full red, when a copious sublimate of a white colour came off. Weight, 4·9 mgrms. No further sublimate was obtainable up to an orange-yellow heat.

There can be little doubt that the iron-black sublimate is the monoxide, TeO, and that the white sublimate is the dioxide, TeO_2. On this view 5·3 mgrms. of Te have been obtained. By difference (Au, Ag) = 3·9 mgrms. The formula affords Te = 5·6, (Au, Ag) = 3·6 when Au : Ag = 1 : 1.

This experiment suggests that a part of the Te is more loosely combined than the rest, and hence passes into that oxide which is formed at the low temperature. It may be that this part is associated with one of the two metallic elements present. The proportions in which Ag and Au occur in sylvanite vary considerably; the gold being, however, always predominant in weight. This would imply that a selenide of silver represented the more unstable body. Some confirmation of this is found in the fact that at the conclusion of the first heating the appearance of the residue suggested the complete separation of the metallic silver; there was less evidence for the separation of gold. At the conclusion of the experiment the latter element is abundantly present. The silver appears as a brilliant frosting, the gold in fibres, and, perhaps, crystals.

Bornite, Cu_3FeS_3 (variable). Weight, 25·6 mgrms.

At lowest red heat SO_2 emitted; recognised by the odour. Oily drops were formed on the glasses. (This liquid was found to be a strong acid, and is doubtless H_2SO_4, the water being obtained mainly from the atmo

sphere). The residue fuses, and gives off no further sublimate up to a bright yellow heat. Loss of weight found to be only 2 mgrms.

Bornite (as above).—The last result suggested a gain in weight by the oxidation of the residue. To test this another quantity (18·5 mgrms.) was roasted on a weighed ribbon in free air. The result was an increase of weight by a fraction of a mgrm. This substance should be dealt with in the absence of oxygen.

Realgar, As_2S_2.—Although heated at a very carefully graduated temperature, the substance did not appear to decompose generally into S and As. There was some liberation of S, however, the characteristic odour of SO_2 being detectable. As the heating continued the remarkable effect was observed of a deposit of what was evidently orpiment on the upper glass and of realgar on the lower. Examination with the microscope showed that the minute globules composing the realgar were, in general, considerably larger than those composing the orpiment. There were also beads of a black vitreous substance on the ribbon; probably As. There has therefore been a loss of S and some separation of As, and a re-distribution of the S, so that the trisulphide, As_2S_3 (orpiment), is formed along with the realgar. The gravitational separation of the two sulphides is remarkable.

Embolite, Ag (Cl, Br).—This melted to an oily brown liquid which appeared to sublime bodily. The whole of the sublimate was easily soluble in strong ammonia. The platinum was left clean.

Tetradymite, $Bi_2(Te,S)_3$.—Bi, 51·9; Te, 48·1; S, small in amount or absent. Weight taken, 27·1 mgrms.

1. Black-grey sublimate formed at a sub-luminous temperature. It was allowed to collect for ten minutes. Weight, 2·3 mgrms.

2. No further black sublimate could be obtained at the former temperature. Raised to a full red, a white sublimate collected. The sublimate after twenty minutes' heating was removed and weighed; weight 6·4 mgrms.

If the black sublimate be TeO and the white be TeO_2, the weight of Te is 7·3 mgrms.

The residue on the ribbon was of a yellow colour, and was fluid at the final temperature. The weight of it was found to be 24·7 mgrms. Assuming that it is Bi_2O_3 the weight of Bi is 22·2 mgrms. The added weights are about 8 per cent too great. As for the proportions, the mineral is variable in composition, and species exist closely resembling it in appearance which are also bismuth tellurides but with largely preponderating amounts of bismuth; *e.g.*, josëite and wehrlite.

Smaltite, $CoAs_2$.—Co, 28·2; As, 71·8. Weight taken, 15·2 mgrms.

A white sublimate at very low red heat. The lower glass broke before the experiment was quite completed. Weight of sublimate, 9·8 mgrms. This is As_4O_6, and contains 7·3 mgrms. of As, or 49 per cent. This being too little according to the formula, a second experiment was made on the same specimen:—

Smaltite, as above; weight taken, 25 mgrms. Care was taken to complete the sublimation. Result, 54·4 per cent of As.

Hence the first experiment is sustained. A borax bead made with the residue on the platinum gave a muddy brown colour. The substance, although labelled smaltite and greatly resembling that ore, cannot be the cobalt arsenide. This specimen was from the collection in Trinity College. It was resolved to try one from another source.

Smaltite, specimen recently purchased from an American dealer, and labelled with the formula $(Co,Ni)As_2$, which should give the same proportion of As as before.

Weight taken, 22·1 mgrms. Total weight of sublimate obtained after raising to a yellow heat, 15·6 mgrms., or 11·8 mgrms. of As. This is 54 per cent. The weight of the residue was found to be 12·4 mgrms. This, which is black in colour, is doubtless Co_3O_4 mainly, and contains about 9·3 mgrms. of the metal. The added weights come to 21·1 mgrms. It is noteworthy that this corresponds very nearly to the formula (Co,Ni)As. It seemed possible that these smaltites correspond to the varieties having the formula $RAs + RAs_2$ which have been recorded with as little as 58 per cent of As. As it was desirable to deal with a more normal specimen, one was chosen which gave the characteristic cobalt bead with borax.

Smaltite highly cobaltiferous. Weight taken 14·7 mgrms. As in the case of the other smaltites there was some deflagration at very low red heat, and a copious sublimate collected. This white sublimate weighed 13·2 mgrms., and contained 10·1 mgrms. of As. The weight of the residue, which was a very dark ash-red colour, was 7·2 mgrms. If this is Co_3O_4 it contains 5·4 mgrms. of Co. The added weights amount to 15·4 mgrms., and the As found was just 70 per cent of the weight dealt with, and therefore agrees with the formula.

Molybdenite, MoS_2.—S, 40; Mo, 60.—Weight taken, 20·8 mgrms.

Having found by trial that only SO_2 was evolved at a low red heat, the substance was roasted with the upper glass removed. A crystalline residue of MoO_3 remained on the ribbon. This was swept off and weighed: = 19·1 mgrms. Hence, Mo = 12·7 and S = 8·1 by difference. The formula gives Mo, 12·5; S, 8·3

Argentite, Ag_2S.—Ag, 87·1; S, 12·9. Weight taken, 14·1 mgrms.

At a cherry-red heat SO_2 escaped and Ag was left. This was swept into the lower glass, and any still adhering silver sublimed off the ribbon. Weight of Ag = 12·4, and, by difference, S = 1·7. On the formula Ag = 12·3; S = 1·8.

These few initial results will be sufficient to illustrate the applications and uses of the apophorometer. I do not think there is any doubt that for rapid determination of mineral species it will be found of use. Percentage estimates as cited above would take many hours to obtain by the ordinary processes of chemical analysis. A good result can easily be obtained in an hour by the apophorometer, and on a very few mgrms. of material. A very large number of mineral species may be partially analysed by its means, and, by weighing and qualitatively testing the residue, complete analyses can, in many cases. be obtained to a degree of accuracy sufficient for determining the species or investigating new ones.

But it will, I think, be found that something more than the discrimination of substances, mineral or other, may be accomplished with it. We can by its means determine the relative stabilities of the constituents of many volatile compounds at high temperatures. It is not improbable that light will in this way be thrown on the internal constitution of the substance. An instance in point seems to be forthcoming in the case of the tellurides dealt with above.

With further experience there will be more to be said about the uses of this instrument. I hope to deal with its applications in a more systematic way in another paper. The temperature at which the sublimates are given off should be determined. It will probably prove of value both in identifying the nature of the sublimate and of the substance under investigation. In my earlier work, before I used the expansion of platinum (as in the meldometer) and employed carbon or platinum for the hob, I determined temperature by optical pyrometry or by electrical resistance. The first method has the fatal objection, as regards the apophorometer, that some of the most useful temperatures are sub-luminous. The second is very troublesome. In the case of the apophorometer I find the readings of the ampèremetre afford the temperature to a sufficient degree of accuracy. It is only requisite to use in every case platinum or carbon of the same length and cross-section. In the case of platinum this, I find, presents no difficulties. By observation of the melting of a few substances of known melting-point, placed on the hob under exactly the same

conditions as obtain when an ordinary experiment is being made, and simultaneous observations of the current, a graph is readily constructed which gives the approximate temperature corresponding to any strength of current. With the watch-glasses in position the graph is a straight line. This much facilitates its determination and use.

The uses of the apophorometer are not by any means restricted to gravimetric measurements. All that class of work which I formerly carried out on the various forms of the meldometer, and which does not call for microscopic observation and accurate temperature readings, can be effected by its means.

(Note.—Some of the original forms—quite simple apparatus—have been occasionally in use in my laboratory since 1886. Among these one form of the instrument, specially constructed for use with carbon, enables sublimation or melting to be observed at very high temperatures and in indifferent gases. Another form enables these effects to be obtained *in vacuo*. The apophorometer combines the advantages of these, and, in addition, enables quantitative results to be obtained. It is made by the Cambridge Instrument Company. The carbon or platinum meldometer was provisionally protected by me in 1886. This protection has, of course, long since expired).

The brief summary of this work, which appears in a former paper (Joly, "The Uses of the Meldometer," *Proc. Roy. Irish Acad.*, May, 1891, [3], xi., p. 44 *et seq.*; and Chemical News, 1896, lxxiii., 93), may be reprinted here; for although other work on the meldometer has been since carried out in my laboratory and elsewhere, this subsequent work has, so far as I know, been largely restricted to the revision of melting-points. The earlier summary of qualitative work is, I think, still fairly comprehensive. In what follows we may read at pleasure "apophorometer" for "meldometer."

(To be continued).

ARSENIC IN ZINC.

By SIDNEY CROOK, late of Public Analyst's Office, Swansea.

Granulate sample through 24 hole sieve, being careful not to introduce arsenic during this operation.

Fit up a Marsh apparatus with a ¼ inch glass tube containing a roll of lead acetate paper and about 6 inches of fused $CaCl_2$ broken to the size of sweet-pea seed, and also a mirror tube. The hole of the inlet tap of apparatus should be about ⅛ inch in diameter. Place 20 grms. of arsenic-free zinc in apparatus, and add 30 cc. of recently boiled and cooled dilute H_2SO_4, which must also be arsenic-free. Acid of suitable strength can be made by adding four parts water to one part H_2SO_4. Test issuing gas for oxygen, and when free and action nearly ceased in flask drop 0·5 grm. sample into the Marsh thistle funnel, into which about 20 cc. of recently boiled and cooled distilled water had been previously poured. Put out hydrogen flame, and place a small lighted Bunsen burner beneath centre of mirror-tube, and when tube is nearly red-hot place the thumb over outlet of mirror-tube to cause a gentle back-pressure. Now carefully open the tap of thistle funnel, and when whole of sample has fallen into flask immediately shut off tap. Remove thumb from outlet, and re-light hydrogen. Practically no water will enter flask, but it will prevent the admission of the slightest trace of air. Draw the water out of funnel with a pipette and replace it with 30 cc. H_2SO_4 as before. Open tap and allow sufficient acid to run in as will keep the flame not more than ¼ inch in height. Continue the reaction for half-an-hour, remove burner, allow tube to cool, and compare mirror obtained with a set of standard mirrors previously prepared. Suitable mirror-tubes can be made out of ¼ inch Jena tubing, and should be about 8 inches long. Suitable standards are 1/5 mgrm., 1/10 mgrm. and 1/20 mgrm., but it is better to arrange weight of sample to give not more than 1/10 mgrm.

LIQUEFIED PRODUCTS FROM NATURAL GAS: THEIR PROPERTIES AND USES.*

By IRVING C. ALLEN and GEORGE A. BURRELL.

Introduction.

The chief purpose of the fuel investigations being carried on by the Bureau of Mines is to increase efficiency in the production and use of the mineral fuels in the United States. One of the investigations has for its object the determination of the economic value of the petroleums and natural gases, with special reference to the supplies in the public lands and the ascertaining of how these resources can be utilised in the industries with least waste and greatest efficiency.

In some of the petroleum fields, particularly in new fields, where the yield of oil and gas is abundant and the methods of handling are necessarily crude, considerable quantities of oil and great quantities of gas are wasted in various ways. In the older fields, where effective methods of handling and storage have been more fully developed, the loss is less.

Yet in almost all the petroleum fields of the country more or less natural gas has been allowed to escape without restraint, and at some places enormous quantities have been wasted. Even to-day, in practically every oil-field of the country, one can see many gas torches needlessly burning the entire twenty four hours.

The handling of oil will not be discussed here. The handling of gas is a difficult matter, and consequently efforts at proper conservation have not as yet been entirely successful. In some fields the loss of gas is due to the fact that a ready market for the gas is not available or to the fact that the yield of the wells has declined so much that transportation of the gas through pipe lines is not profitable.

Natural gas may be divided into two great classes, (1) a so-called "dry gas," known and used for many years as the natural gas of commerce, and (2) a gas containing easily liquefiable vapours, which is known in the vicinity of the oil-fields as a "wet gas." The latter class forms the basis for the so-called "natural gasoline" industry.

Acknowledgments.

The authors wish to express here their appreciation of the courtesies extended to them by the Bessemer Gas Engine Co., of Grove City, Pa., for the use of its plant at Follansbee, W. Va., and to Mr. Frank P. Peterson, of Mercer, Pa., and Mr. O. J. Dougherty, of Steubenville, Ohio, for valuable suggestions and aid.

Commercial Fractions of Natural Gas.

By fractionating natural gas, either during or after liquefaction, four products can be commercially obtained. Roughly, these four products may be described as follows: (1) The gaseous product, the common natural gas of commerce; (2) the semiliquid product, known as the new "wild" product, which should be used only as a liquefied gas and should be held in high-pressure steel containers only; (3) the light liquid product, or light gasoline, used for blending with heavy naphthas; and (4) the heavy liquid product, or ordinary high-grade gasoline.

The first product, natural gas, is discussed in a subsequent section, as are also the third and fourth products.

The possibility of handling the second product in the way that Pintsch and Blau gases are handled, enabling small towns, hotels, and country estates to have the advantages of gas illumination, manifestly opens a new field of comparatively great importance in the natural gas industry, and should add materially to the investments made in the so-called "natural gasoline" industry.

* *Technical Paper* 10, Department of the Interior Bureau of Mines, Washington.

TABLE I.—*Properties of certain Manufactured Gases.*

Name of gas.	Specific gravity (= 1).	Heat value in B.T.U. per cubic foot (0° C. and 760 mm. pressure).	Candle-power (British), burning 5 cub. ft. per hour.	Unsaturated hydrocarbons (per cent).	Saturated hydrocarbons (per cent).	Hydrogen (per cent).	Carbon monoxide (per cent).	Carbon dioxide (per cent).	Oxygen (per cent).	Nitrogen (per cent).	Explosive limit. High.	Explosive limit. Low
Pintsch gas (*a*)	—	(*b*) 1500	45—50	35·65	45·37	12·44	0·60	0·74	2·00	3·00	—	—
Coal gas (*c*)	—	630	16	8·0	34·0	47·0	9·0	1·1	0·0	2·3	7·1	19·0
Acetylene (*d*)	—	1555	150	—	—	—	—	—	—	—	3·0	81
Carburetted water gas (*e*) ..	—	—	22	12·83	14·78	35·17	33·92	1·54	0·0	1·76	—	—
Uncarburetted water-gas (*f*)	—	—	—	—	0·10	51·89	40·08	4·80	–	3·13	—	—
Ordinary natural gas (*g*) ..	0·64	1189	—	—	99·00	—	—	—	—	—	5·5	12·0
Liquid natural gas (*h*).. ..	1·25	(*i*)1800—3300	45—50	—	99·00	—	—	—	—	—	3·0	7·0
Manufactured oil gas (*k*) ..	0·494	633	23	5·85	40·80	39·49	4·50	2·75	0·85	6·01	—	—

(*a*) H. F. Hills, "Gas and Gas Fittings," 1902, p. 52.
(*b*) Approximate.
(*c*) G. A. Burrell, average result of several analyses of coal gas.
(*d*) W. J. A. Butterfield, "The Chemistry of Gas Manufacture," 1898, p. 393.
(*e*) W. J. A. Butterfield, "The Chemistry of Gas Manufacture," 1907, i., 224.
(*f*) V. B. Lewes, "Liquid and Gaseous Fuels," 1907, p. 220.
(*g*) G. A. Burrell, average results of several analyses of West Virginia and Western Pennsylvania gases.
(*h*) G. A. Burrell.
(*i*) Calculated.
(*k*) I. C. Allen, average results of several analyses of manufactured petroleum gas used on the Pacific Coast.

THE DEVELOPMENT OF GAS LIQUEFACTION BY PRESSURE.

The liquefaction of gases by pressure is not a new industry, but only recently has its application to natural gas been recognised as practicable. Before discussing in detail the second, or semiliquid, product mentioned above a brief reference to the industry of manufacturing liquefied or compressed gas is deemed necessary.

In the early seventies, J. J. Coleman successfully liquefied by pressure and cold the gases made by cracking the shale oils of Scotland. ("An Apparatus for the Continuous Liquefaction of Volatile Gases Generated from the Distillation of Bituminous Shale," CHEM. NEWS, Feb. 28, 1879, xxxix., 87; "Mechanical Refrigeration," vol. ii., reviewed in *Sci. Am.*, 1911, civ., 27, and in *Oil and Gas Journal*, June 1, 1911, ix., 4).

By the processes of—

Blau—"Herstellung eines Leuchtgases aus Destillatgasen" (German patent 158198; *Zeit. Angew. Chem.*, 1905, p. 671; "Blaugas," *Seifens Zeit.*, 1907, p. 804; German patent, 1905, 175846; F. Kruger, "Blau Gas," *Chem. Abs.*, 1908, ii., 3402);

Pintsch—W. J. A. Butterfield, "Gas Manufacture," 1907, i., 230—231;

J. L. Gray, "Apparatus for Recovering Light Oils from Natural Gas," U.S. Pat. 933976, 1909;

Hastings-Brink—D. Hastings and A. W. Brink, "Cooling Gas and Obtaining Gasoline" (U.S. Pat. 883640, March 31, 1908, *Chem. Abs.*, 1908, ii., 2447);

The Swiss Liquid Gas Co.—R. E. Mansfield, "Manufacture of Liquid Illuminating Gas in Switzerland" (*Chem. Eng.*, x., 122; *Chem. Abs.*, Jan. 10, 1910, iv., 102);

W. P. Schneider—"Gas-liquefying Apparatus for Demonstration Purposes" (U.S. Pat. 984030, Feb. 14, 1911; *Chem. Abs.*, April 20, 1911, v., 1353);

C. H. G. Williams—"Liquid Hydrocarbons from Compressed Petroleum Gas" (*Jour. Soc. Chem. Ind.*, Aug. 29, 1884, iii., 437);

L. Wolf—"Liquefied Oil Gas" (*Chem. Abs.*, Jan. 20, 1911, v., 372);

Wolski—"Liquefying Natural Gas by the Linde Process" (*Petroleum Rev.*, xiii., 428);

and others gas is made by cracking oils in hot retorts. The gas is then washed and compressed into steel cylinders capable of safely withstanding the pressures developed. Several of these processes for manufacturing gases are commercially successful. They all entail the necessity, however, of first manufacturing the gases and then washing them.

The properties of the better known and more widely used illuminating gases are given in Table I.

The illuminating values there given are those of the ordinary naked flame, without a mantle. How greatly a mantle increases the light is shown in Table II. (H. F. Hills, "Gas and Gas Fittings," 1902, p. 106):—

TABLE II.—*Comparative Illuminating Power of Gas Burners.*

Flat flame burning 5 cubic feet per hour. British candle power.	Burner equipped with mantle, burning 5 cubic feet per hour. British candle power.
23·1	117·3
17·9	90·3
16·2	87·9
14·6	84·4
13·5	81·9

According to A. C. Humphreys (lectures on "Illuminating Engineering," delivered at the Johns Hopkins University, October and November, 1910, under the joint auspices of the University and the Illuminating Society, 1911, p. 208), "The use of mantles in the Pintsch system increased the lighting effect about four times, and with the same storage capacity the length of period between fillings was increased 60 per cent."

Acetylene has been burned with increased efficiency in mantles, but because of the high luminosity and whiteness of the flame itself and because of obstacles yet to be overcome in using mantles, the use of mantles with acetylene has not been generally adopted.

According to tests conducted by Drs. F. Schniewind, Chas. E. Chandler, E. G. Love, and H. Schweitzer (prospectus of the Blau Gas Company, pp. 42—43), Blau gas has a specific gravity of 0·940, a heating value of 1731 B. t. u., and an illuminating value, when burned in an inverted mantle, of 108 standard candles. It is further stated that 2·52 kilogrms. of oil will produce 1 kilogrm. of the gas.

Early Attempts to Liquefy Natural Gas.

The liquefaction of natural-gas products was early recognised as of possible commercial importance.

Pasenmeyer (Frank H. Taylor, "Early History of

Utilisation of Gasoline from Natural Gas," Oil City Derrick, May 6, 1911, p. 9; *Oil and Gas Journ.*, May 11, 1911, ix., 20; "The Gasoline from Natural Gas Industry," *Oil and Gas Journ.*, March 2, 1911, ix., 2—6; *Petroleum*, March 17, 1911, vi., 896) and others procured gasoline in commercial quantities near Titusville, Pa., in 1904, by collecting the condensations in the gas mains. The yield of gasoline so obtained was further increased in 1905 by chilling the pipes with cold water, and from 1905 to 1909 the yield was still further increased by the establishment of small, low-pressure, single-stage compressing plants. In the last few years the industry has made remarkable strides.

Up to the last two years the general practice in the manufacture of liquid natural gas was to make the product by compression of the gas in single-stage compressors operated at a pressure of 150 to 300 lbs. per square inch. The one product thus obtained, so-called "natural gasoline," was run into a tank and "weathered." The weathering consisted in allowing the lighter portions to volatilise spontaneously and escape into the open air until such time as the boiling away of the liquid had practically ceased. Thus the process involved a loss of 25 to 50 per cent, or even more. This loss was an absolute waste, not only of power and of cost of operating the engines and compressors but of the product itself.

Later Improvements.

The next step in the industry was to pass the waste gases (of which only the small quantity used for power had been utilised) from the single-stage compressor through a higher-stage compressor, thereby getting a second and more volatile product—a "wilder" liquid—which was run back into the first tank and mixed with the first or heavier condensate. This mixture was then again weathered to a safe degree, whereby it lost the greater part of the more volatile product that had been condensed in the second stage.

Recently the process has been improved another step, in that the first-stage compressor product is run into one tank and handled as ordinary gasoline; the second-stage compressor product is run into a second tank and handled as a lighter gasoline (Dr. Edwin J. Fithian, "The Fractionation of Natural-gas Gasoline," Natural Gas Association, sixth annual meeting, at Pittsburg, Pa., May 16, 1911, *Natural Gas Journ.*, August, 1911, pp. 16—17), with which the heavy refinery naphthas can be enriched or enlivened.

The last-mentioned method of using the second-stage compressor product should receive wide recognition, and a market for the product should develop that would be no mean factor in the industry. Blending in the proportions of, say, 1 part of the product to 4 or 5 parts of the refinery naphthas makes these heavy naphthas more volatile and of greater value as food for automobiles; it also greatly increases their general usefulness. The proportions to be used in blending, however, must be determined more definitely by test.

Practical Deductions.

The natural gas of this country frequently contains light products that do not condense in the second-stage compressor, and for which it is practicable and necessary to instal three, four, and even higher stage compressors. These light products—true gases at ordinary temperatures and pressures—can be compressed and liquefied, but the liquid gases so obtained must be handled as gases and not as oils. The mistake heretofore made in the "natural gas gasoline" industry, as some have recognised, has been the attempt to handle the light gaseous products as oils and not as gases. Until the manufacturers of this lightest third or fourth stage compressor product recognise its gaseous nature, the absolute necessity for insuring the safety of the public involves certain restrictions in its transportation (see Note), and not until the realisation that this extremely volatile liquid should be handled only in strong steel containers capable of withstanding high pressures will it be transported with safety.

(Note.—B. W. Dunn, "Gas Gasoline Safety Standards," *Oil and Gas Journ.*, June 22, 1911, x., 16–18; "Standards for Gasoline Safety," Oil City Derrick, June 19, 1911, p. 8; "Proposed Regulations of Bureau for the Safe Transportation of Explosives and other Dangerous Substances for the Shipment of Liquids Flashing below 20°F., *Nat. Petroleum News*, February, 1911, ii., 10).

Crude Natural Gas.

Constituents.

The natural gases of the Appalachian oil-fields are not the complex mixtures generally reported, but are composed of the paraffin hydrocarbons with carbon dioxide and nitrogen as impurities. The gases that issue under considerable pressure or that are produced in quantities sufficient to justify piping for distant consumption consist principally of methane and ethane, the methane predominating. Small quantities of the higher paraffin hydrocarbons are also believed to be present. Olefin hydrocarbons and carbon monoxide have not been detected in the samples thus far examined by the Bureau of Mines, and oxygen appears to be present only when the sample has been taken in a faulty manner and air has been admitted.

Natural gases that issue from old wells in which the original rock pressure has diminished contain higher members of the paraffin series, such as propane and butane, in larger quantities, and when a pressure below atmospheric is applied to the wells still larger quantities of the higher paraffins are obtainable. For example, in the oil-pool surrounding Tidioute, Pa., a pool that has produced oil and gas for many years, the gas is now drawn from the wells under a pressure 12 to 13 lbs. below that of the atmosphere, and a liquid product is obtained therefrom without the use of artificial pressure or cooling appliances.

Some natural gases in the United States contain methane only, and such gases are not adapted to the production of gasoline or liquid gas. Gases that contain no paraffin hydrocarbons higher than ethane require a pressure of 600 to 700 lbs. to the square inch at 35° C. for the liquefaction of the ethane. At lower temperatures less pressure would be required. Since these high pressures are not used in the commercial plants producing gasoline from natural gas, ethane is not being liquefied in such plants, but a partial solution of the ethane in those paraffins that are liquefied undoubtedly takes place.

Propane and butane are on the dividing line between gases and liquids and must be handled as such—that is, as heavy gases or as very volatile liquids—and if held must be imprisoned in strong containers only. Pentane, hexane, and heptane are liquids under ordinary conditions and comprise ordinary gasoline.

Present Waste.

The vapours accompanying natural gas are clean and are ready for compression. They are analogous to the manufactured products, but have the great advantage over the latter of being ready made. However, they are at present in a great measure lost to the industries. The vapours should be compressed, as previously stated, but instead of being run into an open tank, or into a closed tank and weathered from it, with a corresponding loss, they should be run into steel containers and held there under compression. Such containers, capable of withstanding 3000 lbs. pressure, may be procured from several commercial firms. They may be transported to wherever gas of high heating or illuminating power is required. Liquefied gases of all kinds, such as carbon dioxide, hydrogen, oxygen, and acetylene, have been handled successfully in such containers for a number of years.

Proposed Utilisation of Products.

Some of the products of natural gas which are now going to waste could be compressed into containers and could be handled as gases. The process has been developed for other gas industries, but its promise as a profitable commercial enterprise in connection with the development of the new product has only recently been recognised.

The multiple-stage compressor may be used for obtaining a number of products, or the single-stage compressor may be used for obtaining one product; then, by allowing this "wild" product to escape from a common container into a second, a third, and a fourth container, under partial pressures, it may be separated or fractionated into a second, a third, and a fourth product. This compression and later separation or fractionation of a common "wild" product into several products is, however, a waste of power, as ordinarily the gas should be compressed through several stages directly into its several products.

(To be continued).

A NEW COLORIMETRIC METHOD FOR TITANIUM.*

By VICTOR LENHER and W. G. CRAWFORD.

THE estimation of titanium is commonly considered by chemists as one of the more troublesome determinations. The methods most widely used exemplify two distinctly different types of chemical action, namely, hydrolysis and colorimetric comparisons. With high percentages of titanium, the hydrolysis of the sulphate is one of the oldest gravimetric methods. The substitution by Gooch (CHEMICAL NEWS, 1885, lii., 55, 68) and Chatard (*Am. Chem. Journ.*, 1891, xiii., 106) of acetic acid solution for that of the sulphate, affords a solution for hydrolysis which gives a far more satisfactory method of separation and precipitation than the older sulphate method. Baskerville's (*Journ. Am. Chem. Soc.*, 1894, xvi., 427) method of hydrolysis in hydrochloric acid has been repeatedly tried out in this laboratory with titanium-bearing material carrying very low percentages up to pure rutile, and uniformly excellent results have been obtained as compared with the acetate method.

For low percentages of titanium the colorimetric method first proposed by Weller (*Ber.*, 1882, xv., 2593; see also *Fres. Zeit.*, ix., 41, and ix., 330) is most generally applicable. The method is based on the yellow colour produced when hydrogen peroxide is added to a sulphuric acid solution of titanium. This colorimetric method has found great applicability in the analysis of clays, silicate rocks, and material of this general character low in titanium. The sensibility of the colour to the presence of fluorides is so pronounced that this bleaching action on a titanium solution containing hydrogen peroxide has been proposed by Steiger (*Journ. Am. Chem. Soc.*, 1907, xxx., 219) as a means of estimating fluorides.

Levy (*Comptes Rendus*, ciii., 1075, 1195), in studying some colour reactions of titanic, columbic, tantalic, and stannic acids, found that certain organic compounds containing one or more phenol groups gave deep colorations with these acids. He worked in concentrated sulphuric acid solutions and observed that all of the colorations were destroyed by the addition of a small quantity of water, with the exception of those produced by stannic acid. From the results obtained he suggested a qualitative method for those acids and conversely a method for the detection of certain phenols.

Muller (*Journ. Am. Chem. Soc.*, 1910, xxxiii., 1506) has studied the colorimetric determination of titanium in aqueous solution by means of the colour imparted by salicylic acid, and finds the detection of very small amounts of titanium is thus made possible.

In studying the double fluorides of columbium, titanium, tantalum, and tungsten with various reagents in concentrated sulphuric acid, Hall and Smith (*Proc. Am. Phil. Soc.*, 1905, xliv., 196) give a number of colour reactions for titanium.

TABLE I.

Morphine	Crimson
Codeine	No colour
Brucine	Light red
Phenol	Brick red
α-Naphthol	Green to green brown
β-Naphthol	Coffee brown
Thymol	Garnet
Resorcin	Red brown
Hydrochinon	Crimson
Pyrocatechin	Chocolate
Pyrogallol	Dark red brown
Salicylic acid	Deep red
Meta-oxybenzoic acid	Chrome yellow
Para-oxybenzoic acid	Chrome yellow
Gallic acid	Brick red
Cinchonidine	No colour
Apomorphine	Light red brown
Narceine	Brown
Berberine	Clear brown
Narcotine	Brown
Chromotropic acid	Deep red

Continuing this line of study a number of other substances have been studied with regard to their behaviour with titanium in strong sulphuric acid solution with the following results :—

TABLE II.

Reagent.	Colour produced in 1 minute.	Colour produced in 24 hours.
Codeine	Light amethyst	Darker
Homatropine	Light red	Cherry
Hydrastine	Light pink	No change
Hyoscyamine	Dark brown	No change
Pelletierine	Light yellow	Pink
Physostigmine	Red	No change
Physostigmine salicylate	Rose yellow	No change
Piperine	Brown	Charred
Strophanthine	Light brown	No change
Aspidospermine	Red	No change
Avenin Legumin	Chocolate	No change
Belladonnine	Deep red	Chocolate
Bulbocapnine	No colour	Pink
Colchicine	Yellow, then red	Reddish brown
Collidine	Light brown	No change
Cryptopine	Deep purple	Black
Chelidonine	Deep red	Purple
Chlorogenine	Yellow	Light brown
Conessine	Light yellow	Dark yellow
Colchicine	Yellow	No change
Cotarnine	Red	No change
Delphinine	Dark red	Darker
Duboisine	Pink	Light reddish brown
Erythrophleine	Light red	Darker
Ditamine	Pink	Red
Digitalein	Red	Darker
Emetine	Red	Deep red
Hydrocotarnine	Red	Black
Jaborine	Red	Dark red
Jervine	Brown	Dark green
Lepidine	Light yellow	No change
Pelletierine	Light red	No change
Pseudopelletierine	Light yellow	No change
Daturine	No colour	Pink

No colours are caused by atropine, caffeine, cinchonidine, pilocarpine, cinconine, cocoaine, quinine, scopol-

* Read at the Eighth International Congress of Applied Chemistry.

amine, sparteine, arecoline, anagyrine, cocaethyline, cinchonamine, conhydrine, cysisine, gelseminine, ecgonine, gussospernine, hyoscine, choline, lobeline, tritopine, tropine, taxine, laudanosine, lycoctonine, oxyacanthine, oxysparteine, picoline, protopine, papaverine, quebrachine, sabadilline, sabadine, aporetin, either in one minute or on being allowed to stand twenty-four hours.

The colorations produced by many of the substances worked with are so much more intense than the hydrogen peroxide colour that a number have been tested to ascertain whether the colour is proportional to the amount of titanium present and not affected by an excess of the reagent.

Phenol and titanium in sulphuric acid solution give a deep red colour in strong solution and a yellow red in dilute. A series of experiments were carefully carried out with phenol and titanium in concentrated sulphuric acid solution, and although a colour developed with as small an amount of titanium dioxide as 0·00005 grm., in no case was it found possible to get a solution in which the colour is proportional to the amount of titanium present.

A similar series of experiments carried out with hydro quinon and titanium in concentrated sulphuric acid showed that while it is possible to detect 0·0001 grm. of titanium dioxide by this method, hydroquinon is not a satisfactory reagent for the determination of titanium.

Chromotropic acid in concentrated sulphuric acid solution was similarly found to show the presence of 0·00001 grm. of titanium dioxide, but the colour produced is not a function of the amount of titanium present.

Salicylic acid in concentrated sulphuric acid solution will indicate as small a quantity of titanium dioxide as 0·00001 grm., but here again the colour is not proportional to the amount of titanium present.

A number of alkaloids were likewise tested with titanium in sulphuric solution, and while a number of them showed intense colour reactions, none were found in which the colour produced is proportional to the amount of titanium present.

Thymol and titanium in concentrated sulphuric acid solution give a deep red coloration if sufficient titanium is present, while in dilute solution a reddish yellow colour is developed. The colour produced by the addition of a sulphuric acid solution of titanium is proportional to the amount of the latter present, and can be made the basis of a colorimetric determination.

Thymol dissolves in concentrated sulphuric acid with a slightly yellow colour, which rapidly intensifies as the amount of thymol is increased. This coloration can be avoided if the thymol is first dissolved in a little acetic acid in which thymol is very soluble, or in acetic acid containing 10 per cent alcohol. Sulphuric acid can then be added without the formation of any colour. The solution of thymol in sulphuric acid thus prepared is fairly stable, and if kept out of bright light will not discolour, but if exposed to direct sunlight it will darken in a few hours.

The ratio of thymol to titanium can vary greatly, but it has been found best to have at least 0·006 grm. of thymol present to every 0·0001 grm. TiO_2.

Table III. indicates results obtained in a Soleil-Dubosq colorimeter.

Table IV. represents results obtained on somewhat larger quantities of titanium with a Kennicott-Sargent colorimeter.

Four previously analysed samples of bauxite in which the titanium content had been obtained by the Weller method are compared in Table V. with the thymol method. Samples of 0·3 grm. each were fused with potassium bisulphate for a half hour, after which the fusion was taken up in concentrated sulphuric acid.

Table III.

No.	TiO present (mgrm.).	TiO_2 found (mgrm.).
1.	0·21	0·20
2.	0·21	0·19
3.	0·31	0·30
4.	0·31	0·294
5.	0·40	0·405
6.	0·40	0·37
7.	0·50	0·50
8.	0·50	0·52

Table IV.

9.	1·0	0·9
10.	1·5	1·5
11.	2·1	2·0
12.	2·5	2·5

Table V.

No.	Weller's method.	Thymol method.	
	TiO_2 (per cent).	TiO_2 (per cent).	TiO_2 (per cent).
13.	3·3	3·7	3·4
14.	1·93	2·2	2·1
15.	2·20	2·15	2·28
16.	2·97	2·83	2·95

Effect of Dilution.

Levy noted, when water is added to a titanium solution coloured by thymol, that the colour fades and is essentially destroyed. The following experiments indicate the effect of the dilution of the acid on the apparent percentage of titanium. Five hundred cc. of a standard titanium dioxide solution was prepared with an excess of thymol present. Aliquot portions were taken and a known amount of water was added to each portion. These portions were cooled and diluted to 50 cc. by the addition of sulphuric acid, sp. gr. 1·84. These test solutions were compared in turn with a 25 cc. portion of the original solution, diluted to 500 cc. with sulphuric acid, sp. gr. 1·84. The addition of water has apparently no effect on the colour until a concentration of 79·4 per cent (sp. gr. 1·725) sulphuric acid has been reached, after which the colour fades in a perfectly regular manner. It has been necessary in making this dilution study to cool the solutions to room temperature after the dilution of the acid, inasmuch as a warm solution is much lighter in colour than one of the same strength a few degrees cooler.

Tablr VI.

H_2SO_4 (per cent).	Actual TiO_2 present (mgrm.).	Apparent TiO_2 present (mgrm.)	Apparent TiO_2 present (per cent.
93·05	0·625	0·625	100
87·60	0·625	0·625	100
85·70	0·625	0·625	100
83·32	0·625	0·625	100
82·00	0·625	0·625	100
80·68	0·625	0·625	100
79·36	0·625	0·625	100
77·60	0·625	0·575	92
76·30	0·625	0·537	86
74·51	0·625	0·500	80
73·23	0·625	0·462	74
71·99	0·625	0·412	66
70·74	0·625	0·375	60
68·97	0·625	0·337	54
67·59	0·625	0·300	48

Effect of Temperature.

The fact that a titanium solution coloured by thymol loses some of its colour when heated, and that on cooling the colour returns, has been repeatedly observed. A series of experiments was therefore conducted to determine at how high a temperature such a solution could be heated without change of colour. In each case the solution was heated to the temperature noted, after which it was cooled and compared with a sample of the original solution. It has been found that the colour is not permanently changed until the solution is heated to 100°.

Effect of Fluorine.

Inasmuch as fluorides exhibit the well known bleaching effect on the yellow colour produced by the addition of

TABLE VII.

No.	Room temperature.	Temperature of heating.	TiO_2 present. Mgrm.	Apparent TiO_2 after heating. Mgrm.	Apparent TiO_2. Per cent.
1.	20°	30°	0·625	0·625	100
2.	20	40	0·625	0·625	100
3.	20	50	0·625	0·625	100
4.	20	60	0·625	0·625	100
5.	20	80	0 625	0·625	100
6.	20	90	0·625	0·625	100
7.	20	100	0·625	0·425	68
8.	20	110	0·625	0·250	40
9.	20	120	0·625	0·150	24

hydrogen peroxide to a titanium solution, the action of hydrofluoric acid on the thymol titanium colour was studied. Fluorides or hydrofluoric acid bleach the colour. In this connection it should be noted that from the preliminary treatment of a titanium-bearing material in order to bring it into concentrated sulphuric acid solution, it is practically impossible for fluorides to be present.

TABLE VIII.

No.	TiO_2 present. Mgrm.	Fl_2 present. Mgrm.	Apparent TiO_2. Mgrm.	Apparent TiO_2. Per cent.
1.	0·625	0·26	0·588	95·6
2.	0·625	0·52	0·576	93·7
3.	0·625	0·78	0·448	72·2
4.	0·625	1·04	0·388	62·2
5.	0·625	1·30	0·338	54·1
6.	0·625	1·52	0·301	48·9
7.	0·625	1·82	0·276	44·2
8.	0·625	2·08	0·250	40·1
9.	0·625	2·34	0·213	34·1
10.	0·625	2·60	0·187	30·0
11.	0·625	2·86	0·150	24·0

Effect of Chlorides, Phosphates, Tin, and Tungsten.

Solutions of various strengths containing hydrochloric acid, phosphoric acid, and tin were systematically added to a thymol sulphuric acid solution, and are apparently without any effect on the coloration. Tungstic acid, on the other hand, markedly affects the colour in direct ratio to the amount of tungsten present.

TABLE IX.

No.	TiO_2 present. Mgrms.	WO_3 present. Mgrms.	Apparent TiO_2. Mgrms.
1.	2·2	0·47	2·48
2.	2·2	0·94	2·75
3.	2·2	1·41	3·01
4.	2·2	1·88	3·250
5.	2·2	2·35	3·50

Of the various organic bodies which produce distinctive colorations with titanium in concentrated sulphuric acid, thymol, phenol, hydroquinon, salicylic acid, and chromotropic acid are the most distinctive. For various reasons thymol produces the most satisfactory coloration which can be used for the detection and estimation of small amounts of titanium. The intensity of the coloration produced by thymol in sulphuric acid with titanium is at least twenty-five times as great as that produced in the hydrogen peroxide method; hence the method is applicable to smaller amounts of titanium than can be determined by the Weller method.

The method possesses certain advantages in simplicity and small number of operations. The actual time for the fusion, dilution, and comparison is short. With a standard prepared the actual working time of the method is less than an hour. The only process requiring time is for the sulphuric acid to cool to room temperature, and this can be facilitated by use of a constant temperature bath.

The sample of the titanium-bearing substance is usually most conveniently brought into solution by fusing with potassium acid sulphate. The fusion can be taken up in concentrated sulphuric acid, and after adding an excess of thymol in sulphuric acid, diluted to a definite volume and the colour compared in a colorimeter with a standard titanium solution.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, March 13th, 1913.

Sir ALFRED KEMPE, Vice-President and Treasurer, in the Chair.

PAPERS were read as follows:—

"*A Simple Method of Finding the Approximate Period of Stable Systems.*" By A. MALLOCK, F.R.S.

"*Motion of Electrons in Gases.*" By Prof. J. S. TOWNSEND, F.R.S., and H. T. TIZARD.

"*Self-inductance of Circular Coils of Rectangular Section.*" By Prof. T. R. LYLE, F.R.S.

"*Ammonium Ferrous Sulphate and its Alkali-metal Isomorphs.*" By A. E. H. TUTTON, F.R.S

The author has added this salt to the thirty-six salts of the series—

$$R_2M\left\{\begin{matrix}S\\SeO_4\\Cr\end{matrix}\right\}_2 . 6H_2O$$

which he has previously investigated in a detailed manner, both morphologically and optically. Re-determinations of the volume constants of the analogous potassium, rubidium, and cæsium salts containing ferrous iron as the M-metal have also been made, based upon new determinations of the specific gravities of the crystals of these salts by the Retgers immersion method, in order that comparisons with the corresponding constants of the ammonium salt now described may be strictly valid.

The results are without exception in line with those already published for the double sulphates and selenates containing ammonium as R-base and magnesium and zinc as M-metal, as well also as with those derived from the author's similar investigation of the double chromates of the magnesium group.

The main conclusion is that the ammonium salt of the group is truly a member of the whole isomorphous series—

$$R_2M\left\{\begin{matrix}S\\SeO_4\\Cr\end{matrix}\right\}_2 . 6H_2O,$$

but not of the inner eutropic series. The latter only comprises the salts containing as the R-base the members potassium, rubidium, and cæsium of the same family group of elements, and in this eutropic series the crystallographic characters, both morphological and optical, are functions of the atomic weight of the alkali metal present.

The singular fact is also again emphasised that the molecular volume and the space-lattice dimensions of the ammonium salt are almost identical with those of the rubidium salt containing the same M-metal (in this case ferrous iron). That is, when ammonium ($2NH_4$, ten atoms) replaces rubidium (two atoms) in rubidium ferrous sulphate (the rubidium salt being the central salt of the group as regards atomic weight of R-metal and the morphological and optical constants) there is practically no change in the structural dimensions, whereas distinctly measurable changes occur if the two rubidium atoms are replaced by two atoms of either of the family analogues, the end members of the family, potassium, or cæsium. This curious and doubtless very significant fact has been observed in connection with every ammonium salt yet studied by the author.

"*Re-combination of the Ions produced by Röntgen Rays in Gases and Vapours.*" By H. THIRKILL, M.A.

Measurements, under widely varying conditions, of the coefficient of re-combination of the ions produced by Röntgen rays in gases and vapours have yielded the following results:—

1. Re-combination seems to take place according to the simple law $dn_1/dt = dn_2/dt = -\alpha n_1 n_2$.

2. For a certain range of pressure, the coefficient of re-combination is proportional to the pressure. Departures from this linear law occur at pressures greater than one atmosphere, and it appears probable that, at high pressures, α reaches a maximum value and then decreases. At low pressures also there are indications of departures from a simple linear law.

"*Optical Investigation of Solidified Gases.* III. *The Crystal Properties of Chlorine and Bromine.*" By Walter Wahl, Ph.D.

Crystallised chlorine and crystallised bromine are rhombic. Bromine is strongly pleochroic; chlorine less so. The absorption diminishes strongly when the temperature is lowered. The existence of a complete analogy in the crystalline characters of chlorine, bromine, and iodine has been established.

"*Abnormal Kinetic Energy of an Ion in a Gas.*" By F. B. Pidduck.

The abnormal rate of diffusion of negative ions in dry air, investigated by Townsend, would be explained if the negative ions had a velocity of agitation in excess of that of an equal number of molecules of the gas. The present paper investigates this from the standpoint of the kinetic theory of gases. The problem of the steady motion of a stream of ions moving in one dimension is solved rigorously on the assumption of an inverse fifth-power law of repulsion between ion and molecule, as in Maxwell's second theory of diffusion, the theoretical values of the abnormal kinetic energy being, however, much in excess of those actually observed. It is highly probable that this effect begins at the point where the velocity of the ions under the electric force becomes comparable with the velocity of agitation of the molecules of the gas. The discrepancy between theory and observation is considered, and it is shown that a very slight loss of energy on impact, such as certainly takes place when an ion is formed by collision, is all that is required to reduce the theoretical values to those observed.

NOTICES OF BOOKS.

An Introduction to the Physics and Chemistry of Colloids. By Emil Hatschek. London: J. and A. Churchill.

This book is intended as a brief introduction to the fundamental facts and methods of investigation in this important branch of physical chemistry. The recent invention of the "Ultra-microscope" by Zsigmondy and Siedentopf has not only largely increased our knowledge of colloidal solutions, but the enterprise of the firm of Carl Zeiss in placing this apparatus upon the market has brought the later developments in the study of colloids within the reach of all. The important and almost forgotten researches of Graham, Faraday, and Tyndall have been revived, and by the work of Perrin and others the Brownian movement and ceaseless activity of colloid gold particles and kindred phenomena have become familiar lecture demonstrations. The book is really a development of a course of lectures delivered at the Sir John Cass Technical Institute. Chapter I. commences with a good historical introduction of the work of Thomas Graham and others and the modern developments of the subject. Ultra-condensers, ultra-filters, and methods for calculating the size of particles, are fully described. "Emulsions," "emulsoids," "sols," "gels," and their reactions are discussed, and in Chapter X. the general conclusions to be drawn from the preceding chapters are briefly summarised. The author is to be congratulated upon having produced an interesting and valuable introduction to the study of this important branch of science. For more detailed information the reader is referred to the works of Ostwald and H. Freundlich, of which English translations would be useful.

Illustrated Catalogue of Chemical Apparatus. London: Messrs. F. E. Becker and Co. (W. and J. George, Ltd., Successors).

The above well-known firm have recently issued a new catalogue of chemical apparatus. In the rapidly extending fields of chemistry and physics a catalogue that shall include the latest important appliances for research is both a serious and costly undertaking. Messrs. Becker and Co. appear to have spared no expense in making their list as complete as possible. Among the novelties we note the stereo-pyrometer, with very complete instructions for its use, description and prices of quartz apparatus, appliances for electro-chemical experiments, Ganong's botanical apparatus, and vacuum vessels for liquid gases. The firm have also introduced a series of "Nivoc" blackboard stencils, a development of their notebook stencils, that make it possible to quickly produce good drawings of chemical apparatus for demonstration purposes. The catalogue is well indexed and profusely illustrated.

Theorien der Organischen Chemie. ("Theories of Organic Chemistry"). By Dr. Ferdinand Henrich. Second Edition. Braunschweig: Friedrich Vieweg. 1912.

In the second edition this book has been considerably enlarged and somewhat widened in scope. It gives an unbiased survey of theories of organic chemistry, and will be found a useful outline of the subject both for students and for technical chemists. In order to explainly clearly the basis upon which modern theories have been built up the author goes back to the time of Lavoisier, and describes in the first chapter the development of theoretical views up to the enunciation of the type theories. Present-day problems are clearly put before the reader, and the chapters on Colour and Chemical Constitution and on Modern Electrochemical Views have been brought down to date and very much enlarged. Nef's theoretical views are given a chapter to themselves, and Michael's system and generalisations are also very fully discussed.

Kolloidchemie der Muskelkontraktion. ("Colloidal Chemistry of Muscular Contraction"). By Prof. Dr. Wolfgang Pauli. Dresden and Leipzig: Theodor Steinkopff. 1912. (1 M.).

This pamphlet contains a lecture which was delivered by Prof. Pauli in Vienna in May, 1912, and in which he dealt at some length with the connection between electrical, mechanical, and chemical processes occurring in muscular tissue. The work of earlier investigators, as well as that of the author himself, is admirably explained, and the significance of Prof. Pauli's work is made clear, while the very definite advances which have been made in recent years by the application of the principles of colloidal chemistry to the study of the changes occurring during muscular contraction are described in considerable detail.

Untersuchung und Nachweis Organischer Farbstoffe auf Spectroskopischen Wege. ("Investigation and Detection of Organic Dyes by Spectroscopy"). By Jaroslav Formanek and Dr. Eugen Grandmougin. Part II., Volume II. Berlin: Julius Springer. 1913.

The second part of Volume II. of this work contains the completion of the tables showing the spectroscopic characters of blue organic dyes, with a summary and index, and the similar tables of red dyes, which are divided into nine groups. Solutions in water, ethyl, alcohol, and amyl alcohol are included, and the effects of the addition of hydrochloric acid, ammonia, and caustic potash are tabulated. Lithographic reproductions of the absorption spectra of the groups and of typical individual dyes are also given.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clvi., No. 3, January 20, 1913.

Three Cymenes and Three Menthanes. — Paul Sabatier and M. Murat.—Ortho-, meta-, and para-cymene can be obtained from the corresponding dimethylcresyl carbinols by first dehydrating them by means of thoria. The 2-cresyl propenes thus formed are transformed into the cymenes by hydrogenation over active nickel. The vapours of the three cymenes when subjected to hydrogenation over active nickel at 170—180° are changed into *o*-, *m* , or *p*-menthane.

Action of Mean and Extreme Ultra-violet Rays on Ethyl Aldehyde.—Daniel Berthelot and Henry Gaudechon.—The mean and extreme ultra-violet rays convert aldehyde into acid in absence of free oxygen, and the successive stages of oxidation (alcohol, aldehyde, acid, carbon dioxide) all occur in absence of oxygen. This is a fresh example of the analogies which exist between the chemical reactions of cellular life and those produced by light. Ultra violet light of wave-length less than 0·25 μ causes rapid polymerisation of aldehyde, and the mean and extreme ultra-violet cause resinification. The presence of water hinders polymerisation and resinification but favours acidification.

Phenyl-α-oxycrotonic Acid.—J. Bougault.—The action of alkalis or alkaline carbonates on phenyl-α-oxycrotonic amide gives eight definite compounds, six of which are new. One of these contains an ether oxide hydrate of ketone, and has the formula—

$$C_6H_5—CH_2—CH_2—\underset{\displaystyle O}{\underset{|}{C}}(OH)—CO_2H$$

$$C_6H_5—CH_2—CH_2—\underset{\displaystyle O}{\underset{|}{C}}(OH)—CONH_2.$$

When heated it gives another acid amide containing two molecules of water less. With alkalis and alkaline carbonates it splits up quantitatively into 1 molecule of ammonia and 2 molecules of benzyl pyruvic acid.

Succinic Acid Aldehyde.—E. G. Blaise and E. Carrière.—The authors have repeated their experiments on succinic acid aldehyde, since their conclusions have been combated by M. Harries (*Ber.*, xlv., 2583). The results have confirmed those previously obtained, and in particular have shown that the polymer of succinic acid aldehyde is a trimer which melts at 167°.

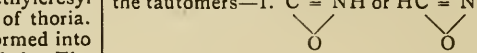
Nitro Derivatives of Oxides of Orthocresyl and Orthocresylene.—A. Mailhe.—The nitration of oxide of orthocresyl in an acetic medium with the application of heat gives the mononitro derivative. When the oxide is introduced gradually into cooled fuming nitric acid the dinitro compound is formed, and on prolonged nitration it yields the tetranitro compound. The nitro derivatives of orthocresylene can be obtained similarly, the mononitro compound being very readily formed.

Atti della Reale Accademia dei Lincei. Vol. xxi. [ii.], No. 10, 1912.

Formation of Compounds of Halogen Salts and Phosphates.—Alkaline Fluorides and Phosphates.—Mario Amadori.—Potassium fluoride and metaphosphate form two compounds, $2KF.KPO_3$ and $KF.KPO_3$. The fluoride and orthophosphate form a compound the composition of which has not yet been determined, while thermic analysis does not reveal the formation of any compound of the fluoride and pyrophosphate. Thus fluorides show a greater tendency to combine with phosphates than with sulphates. Chlorides and phosphates orm no compound s.

Sub-halogen Compounds. — L. Marino and R. Becarelli.—The authors have constructed the fusion-point curve of mixtures of bismuth and iodine in order to ascertain whether the compound BiI_2 is formed. They have found that BiI_3 is the only compound thus obtained, and there are no indications of the formation of a sub iodide.

Tautomerism of Fulminic Acid.—Carlo Palazzo.—From the electrical conductivity of mercury fulminate Ley and Kissel have concluded that fulminic acid can react as the tautomers—I. $C=NH$ or $HC=N$, or II. $HC\equiv N=O$.



This result the author has confirmed by the study of the reaction between sodium fulminate and nitrous acid, and fulminic acid must be regarded as a pseudo acid.

Double Salts of Thallous Chloride and Ferric Chloride with Bismuth Chloride. — G. Scarpa. — Thallous chloride gives with ferric chloride a double salt, $2TlCl.FeCl_3$, and possibly another, $2TlCl.3FeCl_3$. With bismuth chloride it yields three double salts, $3TlCl.BiCl_3$, $3TlCl.2BiCl_3$, and probably $2TlCl.BiCl_3$.

Anodic Oxidation of Ammonia in Presence of Silver Salt.—G. Scagliarini and A. Casali.—Using as anodic liquid a 10 per cent solution of ammonium sulphate saturated with silver sulphate at 15°, and as cathode liquid a 9 or 10 per cent solution of sulphuric acid, the authors have studied the conditions of formation of nitric acid. They find that the temperature has a positive influence, while the influence of the concentration of the ammonium sulphate is negative. There is not perfect proportionality between the duration of the experiment and the yield of nitric acid, which is probably due to the impoverisation of the anodic liquid by the migration of the catalyst to the cathode.

MISCELLANEOUS.

Royal Institution.—On Tuesday next, April 1st, at 3 o'clock, Dr. Arthur Smith Woodward will begin a course of two lectures at the Royal Institution on "Recent Discoveries of Early Man"; on Thursday, April 3rd, Dr. E. Frankland Armstrong will begin a course of two lectures on (1) "The Bridge into Life," (2) "Colour in Flowers"; and on Saturday, April 5th, Mr. Arthur M. Hind will commence a course of two lectures on (1) "Van Dyck and the Great Etchers and Engravers of Portrait," (2) "Rembrandt's Etchings." The Friday Evening Discourse on April 4th will be delivered by Dr. James J. Dobbie on "The Spectroscope in Organic Chemistry"; and on April 11th by Mr. Charles J. P. Cave on "The Winds in the Free Air."

MEETINGS FOR THE WEEK.

TUESDAY, April 1st.—Royal Institution, 3. "Recent Discoveries of Early Man," by Arthur Smith Woodward, F.R.S.

WEDNESDAY, 2nd.—Society of Public Analysts, 8. "Moisture in some English, Colonial, and Foreign Butters during 1910-1912, with a Note on the Mitchell-Walker Moisture Test," by L. Gowing-Scopes. "Egyptian Butter and Semna," by S. H. Trimen. "Simple Test for differentiating between Cocoa-butter and 'Green' Butters," by C. Revis and E. Richards Bolton. "Correct Way to Use Glycerin Jelly in Mounting Microscopical Objects," by L. W. Stansell. "A New Apparatus for maintaining Constant Temperatures," by F. H. and P. V. Dupré.

THURSDAY, 3rd.—Royal Institution, 3. "The Bridge into Life," by E. F. Armstrong, Ph D., &c.

FRIDAY, 4th.—Royal Institution, 9. "The Spectroscope in Organic Chemistry," by Dr. J. J. Dobbie, F.R.S.

SATURDAY, 5th.—Royal Institution, 3. "Van Dyck and the Great Etchers and Engravers of Portrait," by Arthur M. Hind.

THE CHEMICAL NEWS.

Vol. CVII., No. 2784.

MANGANESE IN ORE, FERROMANGANESE, SPIEGLEISEN, &c.

Volhardt's Method.

By SIDNEY CROOK, late of Public Analyst's Office, Swansea.

Weigh out 2 grms. into a 4 to 6 inch evaporating dish covered with a clock glass,, treat with suitable acids, and finally sulphate with 10 cc. concentrated H_2SO_4. Heat until white fumes are evolved, being very careful at this stage to prevent loss through bumping. Allow to cool, carefully take up with warm water, and transfer solution to a flask of about 1 litre capacity, which should afterwards be about half filled with boiling water. Add precipitated ZnO emulsion until all the iron is thrown down, carefully boil, filter (on "Hirsch" funnel preferably), and wash thoroughly with hot water. Remove filter containing residue from funnel, detach residue, and transfer to original flask, the last traces of precipitate being washed off paper into flask with water. Re-dissolve in 5 to 10 cc. concentrated H_2SO_4, re-precipitate with ZnO emulsion, add the whole to main bulk without filtering, cool, pour into a litre measure, and make up to mark. The re-dissolving of residue is very important, as I have found it to contain as much as 2 per cent of Mn. Pipette off aliquot part equal to 0·25 or 0·5 grm. sample into a 1½ litre Jena flask, make up to 600 cc. with water, boil, and titrate with $KMnO_4$ solution (10 grms. per litre) until faint pink colour is permanent and remains so for several hours.

The best way of performing this difficult titration is as follows:—Hold flask containing boiling solution in most dexterous hand, and whirl vigorously but carefully to prevent loss. Now add $KMnO_4$ solution from glass-stoppered burette 2 cc. at a time until pink colour is permanent, when solution clears. Carefully boil emulsion, and violently agitate with constant and reverse whirling for about five minutes, which should be accomplished without loss. If deep pink colour remains pipette off another aliquot part, proceed as before, but stop titrating when burette registers 2 cc. less than previous titration. Boil, and agitate for five minutes as before. Solution on standing will be colourless. Add four drops $KMnO_4$ solution, hold flask in most dexterous hand, whirl flask once towards the body, then immediately away from the body. Do this continuously twenty times, allow to clear, and if supernatant liquor is colourless continue as before with four drop additions till pink colour is permanent. Again boil, and vigorously agitate for five minutes, and continue as above until pink colour is quite permanent. I have seen a faint pink tinge in flask after twenty-four hours. Towards end of the reaction I have found the hardened filters used for strong alkalis very useful in hastening the assay. Filter off about 30 cc. supernatant liquor into a large boiling tube, and compare colour with a standard made by adding two drops standard $KMnO_4$ solution, 10 grms. per litre (about 1/10 cc.) to a litre of distilled water. If filtrate is colourless it is returned to main bulk until end of reaction is reached and colour permanent. After considerable investigation extending over several months I am convinced that vigorous boiling and agitation are absolutely essential to the accuracy of the method, as it is only by these means that the manganese solution mechanically retained by the large precipitate formed during the reaction can be released and accurately determined.

Carried out as described above this is an excellent method, giving accurate results, and infinitely preferable to the tedious and somewhat questionable gravimetric method with its attendant bromine fumes.

A correction for blank should be determined with 600 cc. of the water used (Swansea *tap* water is suitable), 5 cc. concentrated H_2SO_4, and enough ZnO emulsion to just cover the bottom of flask with ZnO after the acid is neutralised in boiling solution.

It is advisable to bind the neck of the titrating flask with a single layer of thick felt or flannel.

THE APOPHOROMETER.*

By J. JOLY, F.R.S., Iveagh Geological Laboratory.

(Concluded from p. 149).

"*Sublimation.*

"This apparatus affords a means of obtaining sublimates much transcending the blowpipe (used either with carbon or aluminium) in delicacy, range, and purity. Sublimates may, in fact, easily be obtained from substances which treated in the blowpipe would appear to afford none, as will appear. The mode of procedure is as follows:—A circular cover-glass—not too thin—grasped in a forceps, is held horizontally above the platinum ribbon, as the temperature is being raised. If the sublimate is one which oxidises, we obtain the oxidised sublimate alone; or the unoxidised sublimate bordered by the oxide, according as we hold the glass further from or nearer to the ribbon.

"The more volatile elements often afford as sublimates both the element and an oxide of it. The elemental sublimate may often be obtained nearly pure by suitably regulating the temperature. Thus, at low temperatures *arsenic* sublimes as a rich grey-black sublimate, showing the mirror when viewed through the glass. At a higher temperature, especially if the glass is held at a distance of 3 or 4 cm. above the ribbon, the white oxide—the trioxide only—is obtained. Sometimes both element and oxide are together on the one glass, affording an 'eye,' the pupil of which is the element. This results from the screening action of the outer parts of the ascending column of vapour, the central parts being, in fact, sublimed in the absence of oxygen, which is all absorbed in the outer layers of the vapour. *Magnesium* affords similar eyes surrounded by the white oxide, or in many cases veiled over by it, so that the dark metal is only seen through the glass. The great avidity of this element for oxygen is shown in this fact. *Tin* also affords 'eyes.' *Thallium* throws a rich black velvety sublimate, fringed with deep ash-red (the oxide?). This is a very beautiful sublimate, but very fleeting, the black soon fading into a pale greyish brown colour. If immediately closed from the air it retains its original tints a longer time. *Cadmium* may also be sublimed as the metal and its oxide. *Indium* affords a white sublimate, dashed with pink and yellow.

"While the metal is thus sometimes obtained with the oxide it more generally affords the oxide only. This is the case, so far as I have observed, with *vanadium*, *lead*, *wolfram*, *bismuth*, *tellurium*, *zinc*, and *antimony*. But, again, sometimes the element appears to sublime without oxidising. Thus *silver* affords a grey-black veil of the metal, iridescent where thinly deposited. *Gold* is also sublimed. *Sulphur* is another case, the oxide being a gas at atmospheric temperatures. *Mercury* gives a sublimate of a grey colour, consisting of globules of the element.

"As regards compounds, the command we have over the temperature in the meldometer enables many very distinct separations to be effected. Thus, dealing with *realgar*, at low temperatures, the substance is sublimed in a rich yellow sublimate. Somewhat higher a decomposition is effected, the free arsenic showing as a white sublimate of the oxide round an eye of sublimed realgar. As the temperature rises the effect is more and more that

* From the *Philosophical Magazine* for February, 1913.

proper to arsenic only, the liberated sulphur not appearing; but the eyes remain most generally distinctly touched with realgar. *Orpiment* behaves in a similar manner. *Pyrargyrite*, a compound of silver and antimony sulphides, throws off the antimony first in a rich white sublimate of the oxide, touched more or less with a pale pink cloud, probably the unaltered compound. A bead of silver is left upon the ribbon, which ultimately volatilises to the grey-black sublimate of silver. *Clausthalite*, the selenide of lead, affords first a sublimate of selenium, a fine ash-red; this then becomes veiled over and intermixed with the rich yellow and whites of the lead oxides, so that a very beautiful marbling is produced, which shows stronger tints of red seen from the back of the glass than from the front.

"Many such effects are seen in a similar order with the blowpipe, but are not produced with the ease, certainty, and cleanliness obtained with the meldometer. Tests may very conveniently be applied to these sublimates as they repose upon the glass, in the knowledge that the only addition to the original substance can be oxygen. Sublimates also may be obtained from very minute quantities of the substance. This is an advantage in more ways than one. . . .

"But the meldometer is capable of affording sublimates which the blowpipe very certainly will not reveal. Thus, for example, *tourmaline* affords a pale whitish-yellow sublimate, the nature of which I have not determined; and *enstatite* volatilises at the highest temperatures obtainable, very nearly, giving a pale brown sublimate. An addition may be made to this form of the meldometer, which will permit of sublimates being obtained in the absence of free oxygen."

[Here follows the description of a closed sublimation vessel with tubulures by which an indifferent gas may be admitted and which has glasses supported both above and below the ribbon for catching the sublimate.] "In this manner sublimates of realgar and arsenic may be made to afford the unoxidised substances."

"*Pyro-Chemistry.*

"Before passing from the subject of the secondary uses to which this form of the meldometer may be put, it remains to add that much of the pyro-chemical work done with the blowpipe may with greater ease and delicacy be effected upon the meldometer. Thus, glasses with microcosmic salt or with borax may be made readily upon the ribbon, the colours produced being well seen, and that, too, however deep in tint, where they thin out at the ends along the bright platinum strip.

"Again, abandoning the use of the ribbon, we may substitute a platinum wire carrying a loop at its centre, and clamping it in the forceps, form beads of great beauty of the usual form from the action of the hot wire. These may be observed, under the microscope, while hot. Changes of colour, often so characteristic, are very distinctly observed through the microscope [or lens] directed upon the platinum ribbon. For example, the changes of tint of a glass formed of copper oxide (CuO) with borax, coating the ribbon, as the temperature is *slowly* raised, is from a fine blue through every gradation of tint to a greenish yellow. The command we possess over the temperature enables these successive changes to be very readily observed. Similarly, the oxidising effects of the blowpipe may be obtained by addition of oxidising substances, such as potassium nitrate. Thus, as with the blowpipe, a glass formed of the sesquioxide of cerium and microcosmic salt which is a pale yellow when hot, passing to colourless when cold, may by the addition of KNO_3 be intensified to a vivid yellow when hot to colourless when cold. By the use of reducing agents deoxidation may, of course, be effected. In this way a mixture of cupric oxide with carbonate of soda and cyanide of potassium yields, first the lower cuprous oxide as a transparent red crystalline body, and finally the metal which alloys with the platinum. The most minute quantities may be used."

LIQUEFIED PRODUCTS FROM NATURAL GAS: THEIR PROPERTIES AND USES.*

By IRVING C. ALLEN and GEORGE A. BURRELL.

(Concluded from p. 152).

Experiments in Liquefying Crude Natural Gas.

Experiments in the production of liquid gas were made at an experimental test plant installed by the authors at the compressing plant of the Penn Gasoline Co., Follansbee, W. Va. The test plant consisted of a small gas-engine, a small compressor, cooling coils of ordinary 1-inch iron pipe immersed in a shallow tank for holding the cooling liquid, and a storage tank made of heavy 6-inch steel tubing. Pressures up to 600 lbs. were obtained, and with the use of ice and liquefied gas prepared in the adjoining compressing plant, the product was cooled to 2° C. as it entered the storage tank. The crude gas as it came from the wells was subjected to different pressures and temperatures, and the amount of liquid produced was measured. From lack of an experimental meter of sufficient capacity, no measurements were made to ascertain the quantity of crude gas liquefied. As all the gas was liquefied, excepting a small leakage, it was assumed that the subsequent volatilisation of the compressed product in the laboratory gave this value. Samples of the liquid material were collected in stout steel cylinders, weighed, and passed through a small experimental meter to determine the gas yield per grm. of liquid.

Yield of Liquid Products.

Table III. gives the results of these experiments, in which practically complete liquefaction was obtained:—

Table III.—*Results of Compression and Cooling Tests of Natural Gas.*

Pressure exerted in liquefaction (lbs. per square inch.	Temperature of cooling coil at entrance to storage tank.	Volume of gas per grm. of liquid.
	°C.	Cc.
415	2·0	600·9
430	4·0	—
506	9·1	—
600	77·5	478·1

A pressure of 415 lbs. at 2° C., of 430 lbs. at 4° C., of 506 lbs. at 9·1 C., or of 600 lbs. at 77·5 C., liquefies practically the total volume of the gas being compressed. Assuming the liquid to be a mixture in which the propane and ethane predominate, as indicated below, 1 grm. of liquid will yield 500 to 600 cc. of gas at 0° C. and 760 mm. pressure; that is, 1 gallon of liquid will yield approximately 50 cubic feet of gas.

Properties of Crude Natural Gas and of the Volatilised Liquid Products.

Table IV. shows the composition of crude natural gas and of the volatilised liquid products of compression.

Analysis No. 1 is of the natural gas of Pennsylvania and West Virginia, which is used at Pittsburgh for heating and lighting purposes. This gas is not adapted to the production of gasoline, but the analysis is inserted here for comparison with the Follansbee gas, which was used in the production of gasoline at the plant before mentioned.

Analysis No. 2 shows the composition of the crude natural gas from the wells at Follansbee before being subjected to compression at the commercial plant there.

Analysis No. 3 shows the composition of the gas left after the initial compression of 50 lbs. to the square inch.

Analysis No. 4 shows the composition of the gas left after the final compression of 250 lbs. to the square inch.

* *Technical Paper* 10, Department of the Interior Bureau of Mines Washington.

TABLE IV.—*Properties of Crude Natural Gas and of the Volatilised Liquid Products of Compression.* (G. A. BURRELL, Analyst).

Analysis No.	Kind of gas.	Specific gravity by effusion method (air = 1).	Heating value in B.T.U. per cubic foot (0° C and 760 mm. pressure).	Composition (per cent). Methane.	Ethane.	Propane.	Butane.	Nitrogen.
1.	Natural gas (Pennsylvania and West Virginia)	0·64	1189	83·0	16·4	—	—	0·6
2.	Natural gas (Follansbee, W. Va.)	1·39	2468	—	21·8	77·7	—	0·5
3.	Residual gas after 50-lb. compression product has been removed	1·35	2364	—	34·9	64·6	—	0·5
4.	Residual gas after 250-lb. compression product has been removed	1·15	2008	—	79·4	20·0	—	0·6
5.	Gas from liquefied gas (400 lbs. pressure, 0° C.)	1·01	1808	3·8	95·0	—	—	1·2
6.		—	2066	—	72·5	27·0	—	0·5
7.		1·28	2214	—	52·1	46·9	—	1·0
8.		—	2621	—	1·1	98·0	—	0·9
9.	Do.	1·02	1816	4·7	94·9	—	—	0·4
10.		—	1925	—	89·3	9·9	—	0·8
11.		—	2108	—	67·0	32·5	—	0·5
12.		—	2161	—	59·4	39·8	—	0·8
13.		—	2708	—	—	89·2	9·9	0·9
14.		—	3221	—	—	24·0	75·0	1·0

TABLE V.—*Properties of the Paraffins ordinarily present in Natural Gas.*

Name and formula.	Boiling-point (° C.).(a)	Specific gravity at different temperatures (water = 1).(b)	Specific gravity at 760 mm. and 0° C. (air = 1). (c)	Weight of 1 litre (grms.).	Heating value in B.T.U. per cubic foot at 0° C. and 760 mm. (d)	Illuminating value (British C.-P.).	Liquefaction point (° C.).	Other liquefaction points (° C.).	Calc. vol. of gas (at 60° F. and 30 inches pressure) from one gallon. (f).	Theoretical vol. of air necessary to burn 1 cub. ft. of gas (cub. feet. (f).
Methane, CH_4 .	−160	0·415 at −160° C.	0·5529	0·7150	1065	5·0(g)	−95·5 at 735 lbs.(h)	−73·5 at 835 lbs.(i)	—	9·57
							−81·8 at 807 lbs.(k)	−131 at 98·4 lbs.(i)	—	—
								−12 at 2700 lbs.(l)	—	—
Ethane, C_2H_6..	−93	—	1·0366	1·3404	1861	35·0 (m)	+35 at 664 lbs.(n)	Ord. temp., 690 lbs.(o)	—	—
							+34 at 738 lbs.(p)	−4 at 676 lbs.(i)	53	16·75
Propane, C_3H_8 .	−45 (e)	—	1·5204	1·9659	2654	53·9 (m)	+97 at 647 lbs.(k)	—	45	23·92
Butane, C_4H_{10} .	1	—	2·004	2·5914	3447	—	—	—	37	31·10
Pentane, C_5H_{12}	36·4	0·627 at 14° C.	—	—	4250	—	—	—	31	38·28
Hexane, C_6H_{14}.	68·9	0·658 at 20° C.	—	—	5012	—	—	—	27	—
Heptane, C_7H_{16}	98·4	0·683 at 20° C.	—	—	—	—	—	—	—	—

(*a*) A. F. Holleman, "Organic Chemistry," edited by A. J. Walker, 1910, p. 41.
(*b*) *Idem.*
(*c*) Walther Hempel, "Methods of Gas Analysis." English translation, by L. M. Dennis, 1910, p. 482.
(*d*) Landolt and Börnstein, "Physikalische-chemische Tabellen," 3rd edition, p. 416, by J. Thomsen.
(*e*) Other authorities give −17° C.
(*f*) Charles Hunt, "Gas Lighting," iii. of "Chemical Technology," by C. E. Groves and Wm. Thorpe, 1904, p. 202.
(*g*) L. T. Wright, *Journ. Chem. Soc.*, 1885, xlvii., 200.
(*h*) Landolt and Börnstein, "Physikalisch chemische Tabellen," 1905, p. 185, by Dewar.
(*i*) F. Bernstein, "Handbuch der Organischen Chemie," 3rd edition, i., 101.
(*k*) Landolt and Börnstein, "Physikalisch-chemische Tabellen," 1905, p. 185, by Olszewski.
(*l*) F. C. Phillips, "W. Va. Geol. Survey, Oil and Gas Levels," 1904, i, A, p. 515.
(*m*) P. Frankland, *Journ. Chem. Soc.*, 1885, xlvii., 235.
(*n*) Landolt and Börnstein, "Physikalisch-chemische Tabellen," 1905, p. 182, by Dewar.
(*o*) *Idem*, p. 182, by Olszewski.
(*p*) *Idem*, p. 185, by Olszewski.

This residual gas is turned into the mains for consumption in the ordinary manner. Its high quality is evident, it having almost twice the heating value of the natural gas used in Pittsburgh.

The four analyses next following, Nos. 5, 6, 7, and 8, show the composition of the liquid gas as obtained from the experimental plant erected by the authors at Follansbee. A cylinder of the liquid gas was taken to the bureau laboratories and connected with a small experimental gas meter. The yield of gas was measured and four samples taken at regular intervals. This test was not finished owing to an accident to the meter.

The next six analyses, Nos. 9, 10, 11, 12, 13, and 14, cover the analysis of the gas, from the first portion released to the last that came from the cylinder. The gas was taken from the top of the cylinder, and the first or more vola-

tile portion approximated ethane in composition. The gases next volatilised contained less ethane and more propane, and, finally, in the last portion butane predominated.

These analyses are approximate, and do not give a definite division of the paraffins. No method is known of separating individual paraffins in a mixture of several, unless means be employed whereby the total gas is liquefied and the different paraffins separated by fractional distillation. (Tests of more detailed fractionation are now being made at the Bureau of Mines laboratories.) In gas analysis no absorbent is known that will quantitatively separate one of the paraffins from a mixture of several and not act upon the others; consequently paraffins are determined as a whole by combustion, and their percentage found by a calculation made from the contraction in volume and the carbon dioxide produced by the burning. By this method the two predominating paraffins are shown, but a small quantity of the others which may exist is not made apparent. For instance, the crude gas that the authors compressed, analysis No. 2, is shown to consist of ethane and propane only. That methane and butane are also contained therein is evidenced by analysis No. 5, in the series of four, and analyses Nos. 9 and 10, in the series of six. Undoubtedly pentane and hexane were were also present. Methane was found in the first portions of gas from each cylinder, but was not present as a liquid in the cylinders, because pressures sufficient to liquefy it were not obtained in the experiments. It was simply dissolved to a certain extent in the other paraffins.

The total paraffin hydrocarbons, as shown by the analyses, are correct, but as stated before only the predominating ones are disclosed by combustion analysis. The methods and apparatus used in the analysis of natural gas will be fully described in a forthcoming Bulletin of the Bureau of Mines, entitled "Methods and Apparatus for the Examination of Mine Gases and Natural Gas." The apparatus is believed to be superior to the types ordinarily used for the analysis of natural gas.

With the exception given in the first analysis, the heating values were calculated from the chemical analyses and are gross heating values.

The heating value of sample No. 1, as determined in a Junker calorimeter, checked the calculated heating value within 10 B. t. u. A burner could not be found, however, that would develop the maximum heating value as calculated from the analysis (W. J. A. Butterfield, "The Chemistry of Gas Manufacture," 1907, i., 233), and all of the determined heating values of the remaining samples in the above table were about 300 B. t. u. lower than the calculated values.

For comparison with the analyses described above, the properties of the paraffins ordinarily present in natural gas are given in Table V.

Characteristics of Liquefied Natural Gas.

The liquefied-gas product obtained from the third and fourth stage compressor product previously mentioned (but not the heavier first-stage compressor product, that which ordinarily remains after weathering) begins to boil at about −40 C., and at its boiling-point has a specific gravity of approximately 0·63. Its coefficient of expansion is estimated to be 0·0009 per 1° C. Its specific gravity at 15° C. would, therefore, be approximately 0·57 to 0·58.

When this liquid is confined the pressures generated by increasing the temperature are approximately as given in Table VI.

From the above data the internal pressure generated by this volatile liquid, or the so-called "wild" product, is seen to reach 755 lbs. per square inch at 55° C. This pressure is probably the maximum obtainable with the very light, or "wild," liquefied natural-gas product having a specific gravity of 0·60 at 15° C., or 100° B. at 60° F. The fact that several gases, under pressures in excess of 150 atmospheres, or 2250 lbs. per square inch, are successfully handled in commerce daily and have been so handled for a number of years, and the fact that this "wild" gas generates an internal pressure of only 755 lbs. at 55° C., or 133° F., which would be an excessively high summer temperature, show that the ordinary handling of this liquefied gas in summer as well as in winter is simple and practicable, and can be done with appliances already developed and on the market. The margin of safety is ample.

Table VI.—*Pressures Generated by Heating Gasoline and Confined Liquefied Natural Gas.*

Temperature.	Pressures generated by refinery gasoline (80°B.).	Pressures generated by natural gasoline obtained at—		
		50 lbs. pressure.	230 lbs. pressure.	400 lbs. pressure.
° C.	lbs.	lbs.	lbs.	lbs.
0	0	—	107	360
5	0	9	117	375
10	0	12	130	398
15	0	16	144	423
20	3	20	154	453
25	5	25	175	482
30	10	30	193	510
35	16	34	210	545
40	26	40	231	585
45	41	46	251	630
50	92	52	275	690
55	350	58	—	755
60	—	65	—	—

There is no difficulty nor secrecy in the production and use of the liquefied natural-gas product. The third or fourth stage compressor product must, however, be treated as liquefied gas, and no attempt should be made to handle it as an oil.

It is important to note that many natural gases will not yield liquefied products by compression under commercial conditions, and the prospective investor is therefore cautioned to ascertain the nature of the vapour content of the gas under consideration before investing in an expensive compressor plant.

Efficiency of Liquefied Product for Definite Uses.

Illumination.

When lighted in burners the liquefied product gives a flame much like that of the ordinary natural gas of commerce, but slightly yellower or smokier, and does not burn so readily in burners with lava tips. Its flame in a Bunsen burner is short but very hot, and it burns better in the short inverted Welsbach mantle than in the longer upright mantle. The highest economy in its use for illuminating purposes will be attained with inverted burners provided with mantles, burners of this type being especially adapted for gases of high heating value.

Heating.

The Méker burner, or a similar burner with a small gas orifice and a large air supply, is well adapted for complete combustion of the gas, as is also the Matchlet blast burner. With oxygen in the oxy-gas burner the liquefied product makes a hot, steady flame, and can be used for a number of purposes, such as brazing, and for operations in which intense local heating is desired.

Because of its high carbon content, the perfect combustion of the gas requires considerably more oxygen than the ordinary gas burners are capable of admitting. A cubic foot of ordinary natural gas requires 10 or 11 cubic feet of air for its complete combustion, but propane and butane, the two richest constituents in the liquid gas, require respectively about 25 and 32 cubic feet of air.

This product of natural gas is equal in quality to any of the similar manufactured gases; it is very clean and pure

and can be handled in the same way as they are. The containers can be easily transported, and the turning of their valves makes a supply of gas available. The liquid gas should be used from the bottom of a container, in order that the burners may be supplied with a homogeneous mixture; the gas should not be taken from the top, because with such an arrangement constant adjustment of the air supply is necessary.

Power.

In order to determine the feasibility of using for power purposes the gas under discussion, a short test was made with a gas-engine. A 10-horsepower two-cycle gas engine provided with a Prony brake for absorbing the load, and equipped with the usual electric ignition, was used. The high-pressure cylinder containing the liquid gas was connected through a reducing valve to a small cylindrical receiver, capacity about 3 cubic feet, in which a pressure of about 3 inches of mercury was maintained; from this receiver a pipe connection led directly to the engine. No attempt was made to determine accurately the fuel consumption per horsepower-hour, nor to find the compression best adapted for the fuel, the test being made simply to determine the behaviour of the gas in a commercial type of engine.

The test was of thirty minutes' duration; full load was easily maintained, and there was no difficulty whatever in keeping the engine up to speed. Throughout the test the engine ran easily, giving no indication of overload; there were no back fires nor preignitions. The indications were that the gas would make a satisfactory gas-engine fuel. The brake horsepower (10·69) during the run was calculated from the following data:—

Average revolutions per minute ..	277·7
Length of brake arm (feet)	5·25
Weight of brake arm (lbs.)	36·5
Total weight on scales (lbs.)	75
Effective weight on scales (lbs.) ..	38·5

A cylinder of the liquefied gas was also used for driving a 30-horsepower automobile. A most satisfactory run was made for a number of miles, although no attempt was made to determine the efficiency developed, the only result desired being to demonstrate that the compressed product could be used for automobile propulsion. It was noted that the gas escaping from the container through the regulating valve supplying the engine became chilled and that considerable frost collected over the surface of the valve. This effect would, in general practice, soon freeze the liquid in the valve and clog the pipe entirely. By installing this valve near the engine exhaust the freezing may be prevented.

Handling of Natural-Gas Products other than Liquefied Gas.

High-grade Gasoline.

The third previously mentioned product of crude natural gas, light high-grade gasoline, is a material that by co-operation with the refiners of petroleum, can be utilised for blending with the heavy naphthas, thereby improving the latter and making them more suitable for the propulsion of high-speed automobiles. This use will materially improve the market for the heavy naphthas, and also widen the field of usefulness for the new compression product. The proportions in which the blending should be made to insure some degree of permanency have not yet been established. (The Bureau for the Safe Transportation of Explosives and other Dangerous Articles is now engaged on these tests.)

Ordinary Gasoline.

The fourth product from compressing crude natural gas, ordinary gasoline, may be handled in the usual way, and need not be discussed in this paper.

THE INFLUENCE OF LEAD ON THE FERROCYANIDE TITRATION OF ZINC.*

By VICTOR LENHER and C. C. MELOCHE.

Of all the volumetric methods for the determination of zinc in ores, the procedure as outlined in the "Modified Waring Method" (*Journ. Am. Chem. Soc.*, 1907, xxiv., 265) is by far the most satisfactory for complex ores. The principal service which this method renders is the removal of all of the heavy metals which interfere with the ferrocyanide titration. In many zinc ores, notably those from the Mississippi Valley, the heavy metals which thus interfere are absent, hence the separations called for in this method can be materially simplified.

While it is universally acknowledged that iron must not be present in the ferrocyanide titration for zinc, the influence of lead has been a much mooted question. Beringer ("Text Book of Assaying") gives quantitative data to show that lead gives a higher result. Seaman (*Journ. Am. Chem. Soc.*, xxix., 207) gives data to show the bad influence of lead. Stone (*Journ. Am. Chem. Soc.*, 1875, xvii., 475, 476) is of the opinion that lead alone need not be separated, but that if lead be present the solution must be quite strongly acid. Miller ("Quantitative Analyses for Mining Engineers") indicates conditions which allow for the presence of lead.

With this brief *resumé* of the various statements as to the effect of lead on the ferrocyanide titration for zinc, attention should be directed to the ferrocyanide method for lead itself, as described by its originator Low (*Journ. Am. Chem. Soc.*, xv., 550). In this method the titration of lead acetate is carried out in a solution containing about 2½ per cent free acetic acid. While Low does not in his latest description of the method specifically state that free mineral acids should not be present, yet from the procedure as outlined, namely, solution of lead carbonate in dilute acetic acid, it is inferred that free mineral acid would not be present. As a matter of fact, our experience with the method seems to show that free mineral acids must be absent in the ferrocyanide titration for lead. In other words, even a very small amount of free nitric or hydrochloric acid prevents the formation of lead ferrocyanide, which would render the method worthless.

Galletti (*Zeit. Anal. Chem.*, iv., 213), who devised the ferrocyanide titration for zinc, worked in acetic acid solution. He used no indicator to obtain the end-point. Fahlberg (*Zeit. Anal. Chem.*, xiii., 379) later showed the efficiency of the method in hydrochloric acid solution, using uranium nitrate as an outside indicator, which is the method commonly used to-day.

A number of series of experiments have been made, the conditions being varied as to the character of the liquid titrated.

Lead acetate was titrated with potassium ferrocyanide in the diluted acetic acid solution as recommended by Low. The temperature of titration was 65° and the solution had a volume of 200 cc.

Table I.

Pb present (grm.)	HCl present (per cent).	Pb found (grm.)
0·1947	none	0·1947
0·1947	0·0125	0·1947
0·1947	0·025	0·1947
0·1947	0·125	0·1921 (*a*)
0·1947	0·125	0·1867 (*a*)
0·1947	0·25	0·0000
0·1947	0·75	0·0000

(*a*) Difference dependent to some extent on temperature.

It is apparent that free hydrochloric acid present up to one-eighth of 1 per cent does not notably affect the lead determination, but when present in quantity as low as 1

* Read at the Eighth International Congress of Applied Chemistry.

per cent no lead ferrocyanide is precipitated and no lead is indicated.

Precisely the same order of results occurs when a chloride is added to the acetic acid solution (Table II).

TABLE II.

Pb present (grm.).	NH_4Cl present (grm.).	Pb found (grm.).
0·1947	none	0·1947
0·1947	0·1	0·1951
0·1947	0·5	0·1947
0·1947	1·0	0·1938
0·1947	3·0	0·035—0·088 (*a*)
0·1949	5·0	0·0000

(*a*) Results differing due to temperature change.

It is obvious that the presence of hydrochloric acid or small quantities of chlorides renders worthless the ferrocyanide titration for lead.

In the titration of lead by the ferrocyanide method a solution of uranium acetate is by far the best indicator. The nitrate is unsuitable, inasmuch as it invariably contains free acid.

Mixtures of varying amounts of zinc and lead acetates were titrated in the presence of different amounts of hydrochloric acid and ammonium chloride (Tables III., IV., and V.).

TABLE III.

Acetate solutions of lead and zinc titrated at 70° in a volume of 200 cc. in presence of 10 grms. NH_4Cl and 3 cc. HCl.

Zn present.	Pb present	Zn found.	Error.
Grm.	Grm.	Grm.	Grm.
0·2000	0·0000	0·2000	—
0·2000	0·0431	0·2010	+0·0010
0·1500	0·0862	0·1512	+0·0012
0·1000	0·1292	0·1005	+0·0005
0·0500	0·1723	0·0498	−0·0002
0·0000	0·1758	0·0005	+0·0005

TABLE IV.

Solutions of acetates titrated at 70° in a volume of 200 cc. in presence of 10 grms. NH_4Cl and 6 cc. HCl.

0·2000	0·0000	0·2000	—
0·2000	0·0431	0·2000	—
0·1500	0·0862	0·1502	+0·0002
0·1000	0·1292	0·1005	+0·0005
0·0500	0·1723	0·0498	−0·0002
0·0000	0·1723	0·0005	+0·0005

TABLE V.

Solutions of acetates titrated at 70° in a volume of 200 cc. in presence of 10 grms. NH_4Cl and 12 cc. HCl.

0·2000	0·0000	0·2000	—
0·2000	0·0431	0·2005	+0·0005
0·1500	0·0862	0·1506	+0·0006
0·1000	0·1292	0·1003	+0·0003
0·0500	0·1723	0·0504	+0·0304
0·0000	0·1723	—	—

A number of experiments were next made using solutions containing chlorides only (Table VI.).

In this group of experiments the amount of hydrochloric acid present was varied. All of the solutions were titrated at 70°, had a volume of 200 cc., and contained 10 grms. NH_4Cl.

With large amounts of free hydrochloric acid present, that is, from 12 to 18 per cent, it is impossible to obtain a definite end-point. When no free acid or as little as one-fourth per cent is present, the true end-point in the titration is a matter of considerable uncertainty. An apparent end-point appears, but by continued stirring disappears. This false end-point is due to the hydrosol form of the colloidal zinc ferrocyanide, which with insufficient free acid goes only slowly into the hydrogel form. The true end-point is quickly reached with 1 and one-half per cent of free hydrochloric acid, and is distinct up to as much as 6 per cent free acid.

From Table VI. it is apparent in general, inthe presence of a material amount of free hydrochloric acid, that the presence of lead would never be discovered in the ferrocyanide titration for zinc.

TABLE VI.

Zinc present.	Lead present.	Zinc found.	Free HCl present.	Error.
Grm.	Grm.	Grm.	Per cent.	Grm.
0·1000	0·1133	0·1001	0·0	+0·0001
0·1000	0·1133	0·0999	0·12	−0·0001
0·1000	0·1133	0·1002	0·25	+0·0002
0·1000	0·1133	0·1002	0·75	+0·0002
0·1000	0·1133	0·1000	1·00	0·0000
0·1000	9·1133	0·1001	1·25	+0·0001
0·1000	0·1133	0·0998	1·50	−0·0002
0·1000	0·1133	0·1001	2·25	+0·0001
0·1000	0·1133	0·1006	3 00	+0·0006
0·1000	0·1133	0·1004	6·00	+0·0004
0·1000	0·1133	0·0991	12·00	−0·0009

In the next experiments successively larger amounts of lead chloride have been added (Table VII.).

TABLE VII.

Volume of solution 200 cc. Ten grms. of ammonium chloride, and one-and-a-half per cent free hydrochloric acid present. Titrations made at 70°.

Zinc present.	Lead present.	Zinc found.	Error.
Grm.	Grm.	Grm.	Grm.
0·1000	0·2266	0·1002	+0·0002
0·1000	0·3399	0·1005	+0·0005
0·1000	0·4532	0·1005	+0·0005
0·1000	0·5665	0·1007	+0·0007
0·1000	0·6798	0·1005	+0·0005
0·1000	0·7931	0·1005	+0·0005
0·1000	0·9064	0·1005	+0·0005
0·1000	1·0197	0·1010	+0·0010
0·1000	1·117	0·1003	+0·0003
0·1000	2·234	0·1003	+0·0003
0·1000	3·352	9·1005	+0·0005
0·1000	3·724	0·1003	+0·0003

In our experience the quantity of ammonium chloride necessary to have present can be anywhere from 1 to 20 grms. in a 200 cc. solution. When excessively large amounts are present, 40 grms. or more, the end-point becomes indistinct.

Various indicators have been suggested from time to time to determine the end-point in the ferrocyanide titration for zinc. Our experiments suggest that a 0·9 per cent ammonium molybdate solution is the most delicate of the various indicators proposed, but that it is not widely applicable. Glacial acetic acid, 5 per cent sodium tungstate, cobalt nitrate, hydrochloroplatinic acid, are fair indicators, but not as delicate as uranium nitrate or ammonium molybdate. Of all the indicators used, the 5 per cent solution of uranium nitrate is very delicate and reliable.

Conclusions.

In the ferrocyanide titration for zinc as commonly carried out, lead is without influence.

The ferrocyanide titration for lead should be carried out in acetic acid solution, and the mineral acids must be absent.

In the technical examination of ores for zinc where lead and iron are the only heavy metals present to an appreciable extent, and such is the case with the Wisconsin zinc ores, it is unnecessary to remove the lead for the ferrocyanide titration for zinc. Half-grm. samples of the ore can be dissolved in 10 cc. concentrated hydrochloric acid with the addition of a little nitric acid. To the solution after dilution ammonium hydroxide is added, and the ferric hydroxide and insoluble matter are removed by

filtration. The precipitate is dissolved in dilute hydrochloric acid and re-precipitation by ammonia is effected, the filtrates being united. The solution should now be acidified with hydrochloric acid, and when evaporated somewhat is ready to be titrated.

For titration the solution must be hot, it should have a volume of 200 cc., should contain 6—10 cc. concentrated hydrochloric acid, and 10 grms. of ammonium chloride. The ferrocyanide solution should be of such strength that 1 cc. = 0·005 grm. zinc and the best indicator is a 5 per cent solution of uranium nitrate.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, March 6th, 1913.

Prof. Percy F. Frankland. LL.D., F.R.S.. President, in the Chair.

The President referred to the loss sustained by the Society through death on February 19 of Prof. William Tate, of Sibpur, who was elected a Fellow of the Society on May 15, 1890.

Certificates were read for the first time in favour of Messrs. Alfred Gilbert Dix, B.Sc., 110, Tufnell Park Road, Holloway, N.; Percy Wolmer Hill, 42, Holyhead Road, Wednesbury; Thomas Arthur Holroyd, B.Sc., Carnbuck Club, Perambur Barracks, Madras; John Francis McCann, 2, Prince of Wales Terrace, Sandymount Avenue, Ballsbridge, Co. Dublin; Harry Bertram Maynard, The Park, Kingswood, Bristol; Kali Prosonuo Rai, M.A., 147, Baranoshee Ghose Street, Calcutta.

The following certificates have been authorised by the Council, for presentation to ballot under By-law I. (3) in favour of Messrs. Herbert Garland, Helouan, Cairo; Julien Pierre Frèderic Pougnet, Natal Estates, Ltd., Mt. Edgecombe, Natal; Thomas Watson, 1186, Davie Street, Vancouver, B.C.

Of the following papers, those marked * were read:—

*56. "*Quinonoid Salts of Nitroanilines.*" By Arthur George Green and Frederick Maurice Rowe.

With the object of isolating quinonoid salts of nitroamines (compare *Trans.*, 1912, ci., 2452), the authors have subjected solutions of various nitroamines in dry benzene to the action of sodium ethoxide. Deep orange to red precipitates were obtained with the following compounds:—*o*-Nitroaniline, *p*-nitroaniline, *p*-nitroethylaniline, 2 : 4′-dinitroaniline, 2 : 4 : 6- rinitroaniline (picramide), 2-nitro-*p*-toluidine, 6-nitro-*m*-toluidine, 4-nitro-*m*-toluidine, 4-chloro-2 nitroaniline, 3-chloro-2-nitroaniline, 3 chloro-4-nitroaniline, 2-nitro-*p*-phenylenediamine, 2 nitro-4-acetyl-*p*-phenylenediamine. The following nitroamines gave no precipitates and exhibited no change of colour:—*m*-Nitroaniline, 5-nitro-*o*-toluidine, 3-nitro-*o*-toluidine, 5-nitro-*o*-4-xylidine, and also the *o*-, *m*-, and *p*-nitro-derivatives of dimethylaniline.

It would therefore appear that all primary and secondary ortho- and para-nitroamines give rise to deeply coloured quinonoid salts under the conditions employed, but that no such reaction occurs in the meta-series. Analysis of the products supports the general formula $X\overset{=}{<}\overset{NH}{NO_2Na}$.

In the case of *p*-nitroaniline, two "chromoisomeric" salts were obtained, namely, a red labile form and an orange stable form.

The tendency of nitroamines to form quinonoid salts is further exemplified by the properties of nitro-*p*-phenylenediamine. This compound crystallises from water in bluish red needles, with a dark green reflex, but dissolves in non-ionising solvents with a yellow colour. In the solid state and in its aqueous and alcoholic solutions, which are red, it probably possesses the constitution of an internal quinonoid salt, $NH_3\cdot C_6H_3\overset{=}{<}\overset{NH}{NO_2}$.

Discussion.

Dr. J. T. Hewitt welcomed the sharp distinction between the *o*- and *p*-nitroanilines on the one hand, and *m*-nitroaniline on the other, since *m*-nitrophenol was not so different from *o*- and *p*-nitrophenols in its chemical nature as might be expected; thus the two latter compounds were not reduced to azoxyphenols by sodium methoxide, neither, however, was *m*-nitrophenol.

*57. "*The Existence of Racemic Compounds in the Liquid State.*" By Alec Duncan Mitchell and Clarence Smith.

The method of determining the molecular weight of a pure liquid by the change of its molecular surface energy with temperature has been applied to the problem of the existence of racemic compounds in the liquid state. Since experience has shown that liquid hydrocarbons and esters usually are unassociated, the substances examined are the active and the inactive modifications of pinene and of limonene, and the dimethyl esters of *d* tartaric and racemic acids.

The apparatus described by Hewitt and Winmill (*Trans.*, 1907, xci., 441) has been used, and all measurements of length have been made with a vernier microscope reading directly to 0·01 mm., and by means of a micrometer eye-piece to 0·001 mm.

The values of k for *d*-, *l* , and *i*-pinene (the last being obtained in two different ways) are 2·36, 2·32, 2·36, and 2·33 respectively, the figures in each case being the mean of four values obtained over a range of about 80°. The values of k for *d*- and *l*-limonene and dipentene (the last obtained in two ways) are 2·34, 2·23, 2·29, and 2·26 respectively. Dimethyl *d*-tartrate and racemate respectively give the values 1·99 and 2·03 for k.

The results indicate that the substances examined do not, in the optically inactive form, exist as liquid racemates.

Discussion.

Mr. F. B. Thole pointed out that there was considerable evidence for the existence of liquid dimethyl racemate to a certain extent.

The viscosities of the active and inactive esters were undoubtedly slightly different, whilst Bruni by cryoscopic measurements in ethylene dibromide solution had found indications of the formation of a racemic complex.

The authors appeared to lay particular stress on the absence of variation of K with increasing temperature as indicating the absence of association for K altered considerably with temperature in the case of associated liquids, such as water, acetic acid, and alcohol.

It was questionable, however, whether the molecular complexes present in these liquids were really comparable with racemic compounds. The component molecules of the latter were probably much more firmly united than those forming the complexes in the ordinary "associated" liquids, and the variation of K with temperature would naturally be much smaller when the complexes were comparatively stable.

*58. "*The Vapour Pressures of the Lower Alcohols and their Azeotropic Mixtures with Water.* Part I. *Ethyl Alcohol.*" By Richard William Merriman.

Quicklime made from marble was found to be the most efficient drying agent for ethyl alcohol. The density of dry alcohol, determined by the method recently described (Wade and Merriman, *Trans.*, 1912, ci., 2429) was found to be 0·80628 $0°/4°$. The alcohol, at 100°, has the power of partly dehydrating calcium hydroxide, so that the last fraction in the preparation of dry alcohol should be rejected.

The vapour pressures above 14° were determined by distilling the dry alcohol through an eight-section Young evaporator column, keeping the pressure constant by means

of a manostat (Wade and Merriman, *Trans.*, 1911, xcix., 984). Below 14° another method was used, but the distillation method is the best method for determining vapour pressures if a cold room is available for the lower temperatures. The view was expressed that experimental results should be smoothed by the method of differences, and not by the use of an empirical formula. The results obtained agree closely with those of Schmidt (*Zeit. Phys. Chem.*, 1891, viii., 620). The boiling-point is 78·30°/760 mm., agreeing with Young's value. Ramsay and Young's values (*Phil. Trans.*, 1886, [1], clxxvii., 155) for the vapour pressures below 30° were shown to be somewhat inaccurate, but on being smoothed became almost identical with the results obtained by the author.

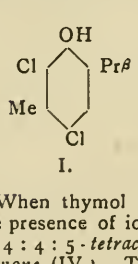
The vapour pressure curves of ethyl acetate (Wade and Merriman, *Trans.*, 1912, ci., 2438) and ethyl alcohol cut each other at a point corresponding with a pressure of 948·1 mm., and a temperature of 84·01°.

The boiling-points of the azeotropic mixtures with water were determined, and compared with the boiling-points of the pure alcohol. The differences between the two series of boiling-points increases with the pressure, as also does the percentage of water.

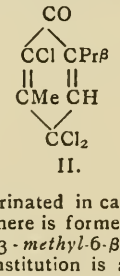
50. "*The Action of Chlorine on Thymol and on* m-*Cresol.*" By HORACE LESLIE CROWTHER and HAMILTON MCCOMBIE.

The authors have investigated the action of chlorine under different conditions and in the presence of various catalysts on thymol and on *m*-cresol.

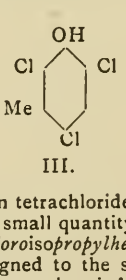
When solid thymol was chlorinated the products obtained were 2 : 6-dichlorothymol (I.), and 2 : 4 : 4-*trichloro*-3-*methyl* 6-iso*propylhexadienone* (II.). The former compound has been described by Blum (*Zeit. Phys. Chem.*, 1892, xvi., 518), and the latter by Lallemande (*Ann. Chim. Phys.*, 1857, [3], xlix., 148), but this author describes it as trichlorothymol. The constitution assigned to it is justified by its liberating iodine from potassium iodide with the formation of 2 : 6-dichlorothymol and the non-formation of acyl derivatives. With sulphuric acid at 100° this compound yields 2 : 4 : 6-*trichloro*-m *cresol* (III.).



I.

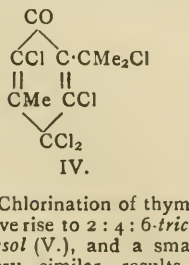


II.

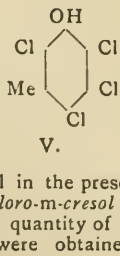


III.

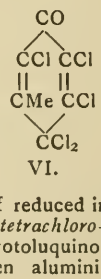
When thymol is chlorinated in carbon tetrachloride in the presence of iodine there is formed a small quantity of 2 : 4 : 4 : 5-*tetrachloro*-3-*methyl*-6-β-*chloro*iso*propylhexadienone* (IV.). This constitution is assigned to the substance because it liberates iodine from potassium iodide, does not form acyl derivatives, and with sulphuric acid yields tetrachloro-*m*-cresol (V.). It was, however, very difficult to arrest the chlorination at this stage, and the main products of the reaction were tetrachloro *m*-cresol (V.), and 2 : 4 : 4 : 5 : 6-*pentachloro*-3-*methylhexadienone* (VI.). In addition there was formed a small quantity of 2 : 4 : 5-trichlorotoluquinone.



IV.



V.



VI.

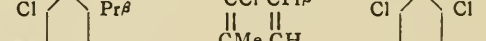
Chlorination of thymol in the presence of reduced iron gave rise to 2 : 4 : 6-*trichloro*-m-*cresol* (III.), *tetrachloro*-m-*cresol* (V.), and a small quantity of trichlorotoluquinone. Very similar results were obtained when aluminium mercury was employed as the catalyst.

m Cresol when chlorinated yielded 2 : 4 : 6-trichloro-*m*-cresol, tetrachloro-*m*-cresol, and 2 : 4 : 4 : 5 : 6-pentachloro-3-methylhexadienone.

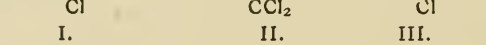
60. "*The Nomenclature of Sugar Derivatives.*" By JAMES COLQUHOUN IRVINE.

At present the position occupied by substituting groups in sugars is indicated by the use of Greek letters, the carbon atom next to the reducing group being termed the α-atom. Attention is now drawn to the fact that confusion arises when, in addition to the position of the substituents, the stereochemical form (α or β) of the parent sugar has also to be included in the nomenclature. Several examples were quoted of cases in which, owing to this difficulty, the names at present in use are either misleading or incomplete.

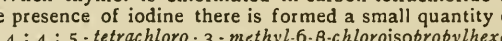
It is now proposed to restrict the use of the expressions α and β, as applied to sugar derivatives, solely to the indication of the configuration of the mutarotatory forms of sugars and derivatives, such as glucosides, which exist in two stereoisomeric modifications. It is further suggested that the carbon atoms in sugars and their derivatives should be indexed by numbers, the reducing group being termed the No. 1 position in the case of an aldose and No. 2 in the case of a ketose. The numerical system may also be applied to polyhydric alcohols, the numeration in such cases being commenced at the terminal primary alcohol group which normally oxidises to give an aldose. The application of the method is illustrated by reference to synthetical aminoglucosides, aminoglucoses, methylated sugars, and a series of mixed ethers derived from mannitol. Examples of the proposed nomenclature are shown below :—



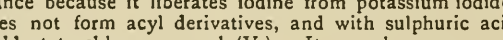
2 : 3-Dimethyl α- or -β-glucose.



6-Monomethyl α- or -β-fructose.



2-Amino α- or -β-methylglucoside.



3 : 4 : 5 : 6-Tetramethyl mannitol.

61. "*Partly Methylated Glucoses.* Part I. ζ-*Monomethyl Glucose and* γε*ζ-Trimethyl Glucose.*" By JAMES COLQUHOUN IRVINE and JAMES PATTERSON SCOTT.

Glucosediacetone when methylated by the silver oxide reaction, is converted into ζ-*monomethyl glucosediacetone* (b. p. 139—140°/12 mm., $[\alpha]_D$ −32·2° in alcohol), and on hydrolysis, ζ-*monomethyl glucose* is obtained. Both the α- and β-forms of the alkylated sugar were isolated, and the mutarotation of each isomeride determined in various solvents. ζ *Monomethyl* α-*glucose* crystallises in rectangular plates melting at 157—158°, and shows the optical change $[\alpha]_D$ +98·6° ⟶ +68·0° in methyl alcohol, whilst ζ-*monomethyl* β-*glucose* forms prismatic needles (m. p. 130—132°), which show $[\alpha]_D$ +29·6° ⟶ +68·0° in the same solvent. These optical values agree only approximately with those calculated according to Hudson's method (*Journ. Am. Chem. Soc.*, 1909, xxxi., 66), but, at the same time, the activity here ascribed to the β-form may not be strictly accurate. Exact agreement with Hudson's figures would demand the alteration of the initial specific rotation of the β-form from +29·6° to +15·1°. The sugar gives a *monomethyl methylglucoside*, and is converted into the same monomethyl glucosephenylosazone previously obtained from monomethyl fructose.

The alkylation of glucosemonoacetone yielded γδε-*trimethyl glucosemonoacetone* as the main product (b. p. 138—139°/12 mm.), from which, on hydrolysis, γδε-*trimethyl glucose* was isolated as a colourless syrup. Contrary to expectation, the equilibrium mixture of the α- and β-forms of this sugar is lævorotatory ($[\alpha]_D$ −8·3° in

water), and so also is the *a*-isomeride. These optical results are quite abnormal, and are being further investigated.

62. "*Partly Methylated Glucoses.* Part II. *βγ-Dimethyl α-Glucose and βγ-Dimethyl β-Glucose.*" By JAMES COLQUHOUN IRVINE and JAMES PATTERSON SCOTT.

The introduction of the benzylidene group into methyl glucoside enables three of the hydroxyl groups of the parent sugar to be protected from methylation. The application of the silver oxide reaction to benzylidene-methylglucoside therefore gave *εζ-benzylidene-βγ-dimethyl α-methylglucoside* (m. p. 122—123, $[\alpha]_D$ +97° in water). Cautious hydrolysis removed 1 molecule of benzaldehyde, with the production of *βγ-dimethyl α-methylglucoside* (m. p. 80—82°), $[\alpha]_D$ +142·6° in acetone), from which, on complete hydrolysis, *βγ-dimethyl glucose* was obtained. Both stereoisomeric forms of the sugar were isolated.

βγ-Dimethyl α-glucose melts at 85—87°, and shows downward mutarotation in acetone solution ($[\alpha]_D$ +81·9° ⇒ +48·3°), whilst *βγ-dimethyl β glucose* (m. p. 108—110°) exhibits mutarotation in the reverse direction ($[\alpha]_D$ +5·9° ⇒ +50·9° in acetone). These values are in good agreement with those calculated by Hudson's method. This generalisation seems, however, to be inapplicable to complexes of the type of benzylidene-methylglucoside.

In connection with the constitution of dimethyl glucose, the influence of configuration in controlling the formation of condensation derivatives of sugars was discussed, and the conclusion was drawn that in benzylidenemethyl-glucoside the aromatic residue occupies positions (ε) and (γ). In the course of the work, a second isomeric form of benzylidene-*a*-methylglucoside was isolated. The new isomeride, for which the name d-*εζ-benzylidene-α-methyl-d-glucoside* was suggested, melts at 148—149°, and shows $[\alpha]_D$ +98° in water.

(To be continued).

PHYSICAL SOCIETY.

Ordinary Meeting, March 14th, 1913.

Dr. A. RUSSELL, Vice-President, in the Chair.

A PAPER on "*Some Oscillograms of Condenser Discharges and a Simple Theory of Coupled Circuits,*" was read by Dr. J. A. FLEMING, F.R.S.

The author gave a very short method, involving only the simplest algebra, for arriving at a formula for the time of free electrical oscillation of a leaky condenser in series with an inductive resistance, the oscillations being damped. The amplitude of the oscillations is proportional to the real part of ω^{jPt}, where $P = p + j\alpha$ and $p = 2\pi n$, n being the frequency and α the damping coefficient. Hence the volt drop down the resistance is $R + jPL$, and that down the condenser is $(S + jPC)^{-1}$. The sum of these two is zero, which leads at once to the equation—

$$P = p + j\alpha = j\left(\frac{R}{2L} + \frac{S}{2C}\right) \pm \sqrt{\frac{1}{CL} - \left(\frac{R}{2L} - \frac{S}{2C}\right)^2},$$

giving the frequency and damping. The formulæ can be confirmed by oscillograms taken at low frequency with a Duddell oscillograph, and a number of these were shown demonstrating the accordance of fact with deductions from the formula. In the same manner the case of the coupled circuits was considered, and the E.M.F. equations written in the form $Tim_1I_1 + jMP_2I_2 = 0$, $jMP_1I_1 + Tim_2I_2 = 0$. When Tim stands for $(R + jPL) + (S + jPC)^{-1}$. Eliminating the currents I_1 and I_2, we have an equation which can be solved for p. Taking the reduced case of non-leaky condensers, tuned circuits, and zero resistance in the secondary, Dr. Fleming deduced the equation—

$$\{p^2CL(1-k) - 1\}\{p^2CL(1+k) - 1\} - \alpha_1^2 CL(1 - (1+k^2)p^2CL) = 0,$$

which shows that there are, in general, oscillations of three frequencies in the circuits. This was confirmed by photographs of oscillograms and diagrams of resonance curves.

Prof. S. P. THOMPSON admired Dr. Fleming's ingenious method, which was, he considered, much more intelligible to students than writing down the differential equation and then integrating it. He also admired the beautiful oscillograms, and hoped it was possible to procure copies of them, as he considered every teacher ought to have a set.

Dr. W. H. ECCLES also expressed the opinion that Dr. Fleming's method of solution would be valuable to teachers. He also pointed out that the leakage S of the condenser could be so adjusted as to neutralise the effect of the external resistance R on the period, and suggested that this fact might be made use of to measure high frequency resistances.

Prof. G. W. O. HOWE stated that he had used a similar method in teaching. It was very important to clearly bring before students what was happening in the various circuits. The oscillograms could be used to determine the high frequency resistance, as the log. dec. of the train of oscillations could be measured very accurately.

The AUTHOR, in reply, stated that he possessed the original copies of the oscillograms, and would be pleased to supply copies to teachers desiring them.

A second paper was read by Dr. FLEMING, describing some Braun cathode ray tubes (exhibited) used as high frequency oscillographs, and also an electrostatic influence machine (exhibited), giving a steady current of 300 to 350 micro-ampères for working them.

The Braun tubes have electrostatic deflection plates in them, and an embracing field coil for providing a longitudinal field to keep the cathode spot in a central position on the screen. The tubes are worked by connecting the deflection plates to the terminals of an alternator, whereby the cathode spot is made to move to and fro over the screen with a nearly uniform velocity. The shaft of the alternator carries a commutator by means of which a condenser is repeatedly discharged through an inductive coil which acts as a deflecting magnet on the oscillograph tube, and displaces the cathode ray at right angles to the direction of the electrostatic displacement. In this way the spot has two motions, a uniform horizontal motion and a vertical oscillary motion, the two being kept in step with each other. Hence a visual representation is given on the phosphorescent screen of the nature of the oscillation. The electrical machine above mentioned, made by Messrs. Müller-Uri, of Braunschweig, was shown in operation, and the current given by it was seen to be sufficient to cause decomposition of acidulated water in a lantern voltameter.

Mr. A. CAMPBELL stated that one German instrument maker had recently described in a paper a method of improving the surface of ebonite. The ebonite was painted with a composition, and then heated to nearly the softening point of the ebonite, when the composition spread over the surface, and produced a surface like amber, which was unaffected by either sunlight or moisture.

Prof. J. T. MORRIS stated that he had employed Braun tubes ten years ago to find the maximum value of an alternating current, but found many difficulties in their use. He would like to know what was the actual voltage on the tube, and also whether the oscillograms were in a continuous line, or were made up of a row of dots showing the cathode rays to be produced intermittently, as he believed was often the case with a Wimshurst machine. His brother, Mr. D. K. Morris, had suggested, several years ago, using a different number of sectors on the two plates in order to overcome this. He would like to know whether anyone had tried it. He asked if a high-potential battery would not give a more satisfactory result than the Wimshurst.

Dr. R. S. WILLOWS asked if Dr. Fleming had used a hot lime cathode, as then the tubes could be run from 200-volt mains, and, as the cathode rays so produced had

a much smaller velocity, much lower voltages could be used in the condenser discharges.

The AUTHOR stated that batteries would be ideal, but the price was prohibitive. Ordinarily Wimshurst machines do give a spotted appearance to oscillograms taken with Braun tubes, but the present machine gave a perfectly uniform and continuous curve. He had never used hot lime cathodes.

A paper on the "*Stretching and Breaking of Sodium and Potassium*" was read by Mr. BEVAN B. BAKER.

The author described how wires made of metallic sodium and potassium collapse when stretched, not to a point, as is the case with most plastic substances, but from two opposite sides only, into a chisel end.

The wires upon which experiments were conducted were made in two ways—firstly, by pressing the metals through a small hole into a bath of paraffin oil to hinder oxidation; and, secondly, by running the metal, molten under oil, into a glass tube, and allowing it to solidify. Wires made by both the above methods showed the same behaviour on stretching.

Wires made by the second process also showed, on extension, two sets of equidistant rings on their surface, each inclined at an angle of 45° to the axis, the rings of opposite sets touching along the line of greatest thinning, and bisecting one another along the line at which no thinning takes place.

Dr. Andrade has also noticed the same effects of breaking and forming rings with wires made of solid mercury.

The author suggested an explanation of the phenomenon, based on the assumption that the portions of the metal brought into play are in the form of cubes. Such cubes when placed so that a plane through two opposite edges was parallel to the axis of the wire would allow of lateral contraction by faces sliding over one another in one direction only, and not in the direction at right angles.

Dr. L. N. G. FILON asked if the section of the stretched wire was accurately elliptical. It was interesting to note that the angle of the rings did not change when the wire was drawn out.

Prof. A. W. PORTER remarked that it looked as if the metal possessed a lattice-like structure.

The AUTHOR stated that he had not measured the sections to see if they were accurately elliptical.

A paper "*On the Latent Heat of Evaporation of Steam from Salt Solutions*" was read by Mr. R. G. LUNNON.

The paper records the results of a research into the latent heat of evaporation of steam from salt solutions.

The experimental method was to supply a measurable quantity of heat electrically, through a small lamp to the solution boiling inside a calorimeter. The latter was placed within a double-walled vessel surrounded by a solution boiling at the same temperature, and the steam from the inner vessel passed out through a tube into a detachable condenser, which was weighed at intervals.

Measurements were made with the solutions of six different salts. Theoretical considerations show that the difference between the measured heat L, and l_T the known heat of evaporation of water at the same temperature, is the heat of solution Q, and the present results indicate that for salts of the same acid Q is proportional to the concentration.

For unsaturated solutions of KCl and NaCl the interesting result is found that the heat of evaporation is approximately constant for all concentrations until saturation is reached.

Mr. F. E. SMITH remarked that in a similar apparatus he had used for the distillation of water he found that priming did take place. It would have been more satisfactory if the author had used a solution of NaCl and tested the distillate for its presence.

The AUTHOR stated that he had tested the distillate in one case, but not with NaCl.

Some Flame Spectra were exhibited by Dr. E. N. DA C. ANDRADE.

If a flame containing a large amount of chlorine be prepared by passing the air supplied to a colourless gas flame over chloroform, wires of certain metals—copper, nickel, iron, for instance—held in the flame give characteristic colorations in the different zones of the flame. These are due to the chlorides of the metal, which can exist undissociated, in some zones of the flame at least, in the presence of excess chlorine. The chloride spectrum of copper is well known (of Smithells), but the chloride spectra of nickel, cobalt, and iron chloride do not seem to have been fully observed before. The method makes it easy to observe the different emissions which take place in the different zones, and also the electrical migration of the vapour discovered by Lenard in 1902. All the chloride spectra have certain common characteristics. Attention is called to the fact, discovered by Smithells, that for the vapours of some metals—*e.g.*, lithium, strontium—the coloration produced in the flame is destroyed by chlorine. In such cases the vapours are not electrically charged, while in the case of the metallic chlorides which give characteristic spectra in the flame the vapours are strongly charged.

By bringing wires into flames containing bromine and iodine compound spectra were observed in some cases.

Mr. A. CAMPBELL asked if Dr. Andrade could give an explanation of the blue coloured flame obtained when NaCl is thrown on to a fire.

The AUTHOR replied that the flame was the spectrum of copper chloride, there being a sufficient impurity of copper in the coal.

Some Spark Photographs at High Pressures were exhibited by Mr. W. B. HAINES.

The photographs were obtained by connecting one terminal of an induction coil to a copper disc covering the back of a photographic plate, while the other terminal was led up to the centre of the film. When a spark is passed by breaking the primary circuit an electric splash can be seen to spread from the terminal over the plate, and an impress of this is obtained on developing. A special pressure chamber was constructed to contain the plate, so that it could be exposed to the spark under a surrounding gas pressure of anything up to 16 atmospheres.

NOTICES OF BOOKS.

Notes on Chemical Research. By W. P. DREAPER, F.I.C., F.C.S. London: J. and A. Churchill. 1913.

THE text of this book has been reprinted from the *Chemical World*, in which it appeared last year in the form of a series of articles. The author discusses the personal qualifications necessary to enable a man to become a successful investigator, basing many of his conclusions upon the consideration of the lives and work of the great pioneers of chemical science. He has valuable suggestions to offer relating to the choice of a subject, both for research work in pure and in applied chemistry, and he gives excellent advice upon the reading of original articles and upon the authorities to consult for special information. The student who is working in a laboratory will gain by reading the book even if he cannot immediately put its precepts into practice. It will widen his outlook and give routine work, which might otherwise become monotonous and wearisome, a new aspect.

The Plant Alkaloids. By THOMAS ANDERSON HENRY, D.Sc. (Lond.), F.C.S. London: J. and A. Churchill. 1913.

THE plant alkaloids are classified in this book in groups according to the nature of the bases from which they are derived, and then sub grouped according to source, all

alkaloids from the same plant being considered together. The alkaloids of unknown composition are arranged in the alphabetical order of the botanical names of the plants from which they are obtained. This system of classification appears to be on the whole, and in spite of some difficulties in applying it, the most satisfactory and convenient. The occurrence, methods of estimation, and chemical and physical properties of each alkaloid are described, and the probable constitution is discussed. Some account is given of the physiological characters and action of the more important alkaloids, and the references to original sources of information are very full and complete. In an appendix some important work which has been finished while the book was in the press is summarised, and miscellaneous alkaloids which have not yet been fully characterised are tabulated, with references and brief notes as to their nature.

Atomprozente und Gewichtsprozente. ("Atomic Percentages and Percentages by Weight"). By Dipl. Ing. Fritz Hoffmann. Halle-a.-d.-S: Wilhelm Knapp. 1912.

In this monograph the author explains the advantages of representing graphically the properties of solutions by means of diagrams expressing the amounts of the elements present as atomic percentages instead of percentage parts by weight. This method of representation, which may find extensive application in the physical investigation of alloys, appears to be specially useful in the case of alloys containing three or more components. Methods of converting the one series of diagrams into the other may depend simply on calculation, or calculation and graphic methods may be combined, or finally a projection method may advantageously be used for multiple systems. All these are very fully explained by the author in language which is as non-mathematical as possible, and the application of them in particular cases is well illustrated by diagrams. The monograph will possess a special interest for chemists engaged in metallographic research, although the same principles of graphic representation may be applied in the investigation of other problems of physical chemistry.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Seances de l'Academie des Sciences. Vol. clvi., No. 4, January 27, 1913.

Application of Stokes's Law to the Fall of very small Droplets and to the Determination of the Charge of the Electron.—A. Schidlof and J. Murzynowska.—The authors have investigated the applicability of Cunningham's correction of Stokes's law to the case of droplets of oil. Among the various liquids used they found that olive oil gave the best results, and they employed drops of diameter from 0·8 to 2·1 microns. The results obtained indicate that Cunningham's theory may be applied to the full of very little drops of oil in air under atmospheric pressure.

Action of Ammonia on Primary Amylamines.—Félix Bidet.—When ammonia gas is allowed to act on isoamylamine hydrochloride the reaction does not begin until fifteen minutes after contact, while with the normal salt it begins at once. The equilibrium pressures are decidedly lower for the normal salt than for its isomer until a temperature of 50° is reached, when they are practically equal. The action may be represented by the equation—

$$2(C_5H_{11}NH_2HCl) + NH_3 = (C_5H_{11}NH_2)_2(C_5H_{11}NH_2HCl) + NH_4Cl.$$

Additivity of Diamagnetism in Combination.—Paul Pascal.—From experiments with tin and mercury it appears that the diamagnetism of the metals is additive in the higher members of the fatty series of organo-metallic compounds. It is difficult to determine the coefficient of magnetisation of a diamagnetic element because of the impossibility of freeing it from iron and other magnetic impurities, but it is much easier to prepare the fatty organo-metallic derivatives in a state of purity and deduce from them the diamagnetism of the metal.

Analysis of Complex Mixtures of Hydrocarbons.—P. Lebeau and A. Damiens.—At 127° a mixture of ethane, propane, and isobutane can be separated by a mercury pump into two portions, one consisting of all the ethane and some of the propane, and the other of the rest of the propane and all the isobutane. These can then be analysed eudiometrically. When vapours of gaseous hydrocarbons, or gaseous hydrocarbons themselves, are present, the mixture is cooled to −78°, and by a first extraction the gaseous hydrocarbons and a small quantity of the vapours of the liquid hydrocarbons are separated. At −100° the pentanes have no appreciable tension, and the gaseous hydrocarbons can be isolated.

Reactions of Sodamide in Presence of Liquid Ammonia.—E. Chablay.—When methyl iodide is allowed to drop into sodamide in suspension in liquid ammonia an energetic reaction occurs, the products being sodium iodide and monomethylamine. With ethyl and higher iodides and chlorides a somewhat less energetic reaction occurs, and the corresponding ethylenic hydrocarbon is evolved. The reaction is analogous to that with caustic potash. Thus—

$$C_3H_7Cl + NaNH_2 = NaCl + C_3H_6 + NH_3$$
$$C_3H_7Cl + KOH = KCl + C_3H_6 + H_2O.$$

Synthesis of Galactosides of Alcohols by means of Emulsine.—Em. Bourquelot, H. Hérissey, and M. Bridel.—β-Propylgalactoside can be prepared by dissolving galactose in propyl alcohol containing 20 per cent of water and adding emulsine. If the liquid is allowed to stand at the temperature of the laboratory for seventy days the galactoside can then be extracted by means of acetic ether. β-Propylgalactoside crystallises in white needles, melting at 105—106°. Its rotatory power in aqueous solutions is −8·86. It reduces cupric solution very slightly. β-Benzylgalactoside can be prepared similarly. After it has been dried *in vacuo* it melts at 100—101°, but the fused product after solidification does not melt before 119—120°. Its rotatory power in aqueous solution is −25·05.

α-Chlorocyclopentanone and its Derivatives.—Marcel Godchot and Félix Taboury.—When dry chlorine is passed over cyclopentanone in diffused light monochlorocyclopentanone is obtained. Its chlorine atom is very mobile, and it is readily hydrolysed in water in presence of barium carbonate, giving the corresponding ketone alcohol. When the latter is oxidised with 1 per cent potassium permanganate at the ordinary temperature glutaric acid is obtained. If chlorocyclopentanone is distilled at the ordinary pressure cyclopentenone is formed; a better yield may be obtained by heating the chlorine derivative in presence of an excess of diethylaniline.

MISCELLANEOUS.

Literary Intelligence.—Messrs. J. and A. Churchill have just ready for publication Volume 7 of the new edition of "Allen's Commercial Organic Analysis." This volume has been re-written under the editorship of Mr. W. A. Davis, B.Sc., and Mr. S. S. Sadtler, S.B. The subjects and authors are as follows:—Vegetable Alkaloids, Ptomaines or Putrefaction Bases, by G. Barger; Gluco-

sides, by E. Frankland Armstrong; Non-Glucosidal Bitter Principles, by G. C. Jones; Animal Bases, by A. E. Taylor; Animal Acids, by J. A. Mandel; Lactic Acid, by W. A. Davis; Cyanogen and its Derivatives, by Herbert Philipp. It will be observed that each contribution is dealt with by an expert in his department. Amongst their Spring publications Messrs. J. and A. Churchill are about to issue:—"Liquid Air Oxygen Nitrogen," by M. Georges Claude, Engineer Laureate of the Institute of France; translated from the French by Mr. H. E. P. Cottrell. Considerable attention is being devoted to Nitrogen owing to its demand by agriculturists. The work contains 150 illustrations. "The Examination of Waters and Water Supplies," Second Edition, by Dr. J. C. Thresh, Medical Officer of Health for the County of Essex. The new edition has been amplified and many new illustrations added to bring it up to present-day standard. "A Laboratory Text-Book of Chemistry," Part I, by Mr. V. S. Bryant, Assistant Master at Wellington College. For use in schools and colleges.

Messrs. Longmans, Green, & Co. have in preparation a series of Monographs on Physics, which will to some extent follow the lines of their Monographs on Biochemistry and on Inorganic and Physical Chemistry. The Editors of the Physical Series will be Sir J. J. Thomson, O.M., F.R.S., and Dr. Frank Horton, of the Cavendish Laboratory, Cambridge. The first volume in the series will be on "Rays of Positive Electricity," by Sir J. J. Thomson.

Molecular Magnitudes of Metals in Solid Phases.—M. Padva and F. Bovini.—From cryoscopic experiments performed with solutions of silicon in copper it may be deduced that silicon is monatomic. When from a dilute solution of concentration C_l a solid solution of concentration C_s separates and the ratio C_s/C_l remains constant, it may be deduced that the dissolved substance in the solid state has the same molecular magnitude as in the liquid state. Applying the principle to the case of alloys of tin, cadmium, and bismuth, the authors have shown that cadmium is monatomic in the solid state.—*Atti della Reale Accademia dei Lincei*, xxi., No. 10.

MEETINGS FOR THE WEEK.

MONDAY, 7th.—Royal Institution, 5. General Meeting.
—— Royal Society of Arts, 8. (Howard Lecture). "Aeronautics," by Prof. J. E. Petavel, F.R.S.
—— Society of Chemical Industry, 8. "High Pressure Reactions—the Formation of Coal and of Hydrogen," by Dr. F. Bergius.

TUESDAY, 8th.—Royal Institution, 3. "Recent Discoveries of Early Man," by Arthur Smith Woodward, F.R.S.

WEDNESDAY, 9th.—Royal Society of Arts, 8. "Electric Supply in London," by Frank Bailey.

THURSDAY, 10th.—Royal Institution, 3. "Colour in Flowers," by E. F. Armstrong, Ph.D., &c.
—— Royal Society. "Various Inclinations of the Electrical Axis of the Human Heart," A. D. Waller. "Nature of the Toxic Action of the Electric Discharge upon Bacillus *Coli communis*," by J. H. Priestley and R. C. Knight. "Morphology of various Strains of the Trypanosome causing Disease in Man in Nyasaland—(II.) The Wild Game Strain, (III.) The Wild Glossina Moristans Strain," and "Infectivity of Glossina Moristans in Nyasaland," by Surgeon-General Sir D. Bruce, Majors D. Harvey and A. E. Hamerton, and Lady Bruce.

FRIDAY, 11th.—Royal Institution, 9. "The Winds in the Free Air," by Charles J. P. Cave, M.A.
—— Alchemical Society, 8. (At International Club, Regent Street). "The Evidence for Authentic Transmutations" by M. Gaston de Mengel.
—— Physical Society, 8. "Some Errors in Magnetic Testing due to Elastic Strain," by A. Campbell and H. C. Booth. "Cathodic Sputtering," by G. W. C Kaye.

SATURDAY, 12th.—Royal Institution, 3. "Rembrandt's Etchings," by Arthur M. Hind.

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THE CHEMICAL NEWS.

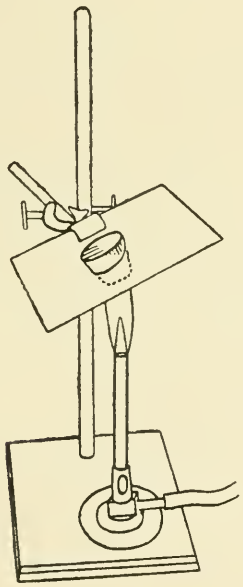
Vol. CVII., No. 2785.

NOTE ON A PERFORATED SILICA PLATE FOR EXCLUDING FLAME GASES FROM A CRUCIBLE DURING IGNITION.

By ALEXANDER CHARLES CUMMING.

The device shown in the accompanying sketch has been in use in the Chemistry Department of the University of Edinburgh for some time. It consists of a silica plate, 5 inches square, with a hole bored in it of such size as to admit a crucible to one-half of its depth. The silica plate is held in an inclined position by a clamp.

By this means the flame gases are excluded from the interior of the crucible during an ignition. With this device calcium carbonate in a platinum crucible is quickly reduced to oxide with a good Bunsen burner, while with a Meker burner the reduction is complete in a few minutes



even when a porcelain crucible is used. The device is also useful for cases such as the ignition of nickel oxide, where there is a danger of reduction. For the estimation of sulphur in coal some such device is absolutely necessary to exclude the flame gases.

The original idea is due to J. Löwe, who used clay discs. Hillebrand (*Bull.* 442 U.S. Geological Survey, p. 32) has suggested the use of an asbestos sheet with a perforated sheet of stout platinum foil in the centre. The silica plate has the advantage of cheapness and rigidity, and has been found in practice to be very useful in quantitative analysis.

The holes were bored on a lathe by means of a copper tube of appropriate size, the cutting end being covered with carborundum and lubricant. Doubtless the manufacturers of silica ware would supply these perforated plates.—*Proceedings of the Royal Society of Edinburgh*, xxii., Part I. (No. 4).

THE PRESENT STATUS OF THE TEMPERATURE SCALE.*

By GEORGE K. BURGESS, Sc.D., Bureau of Standards, Washington, U.S.A.

The past few years have been marked by great advances in the exact determination of the temperature scale in terms of fixed points of melting, transformation, or boiling, of pure substances, extension of the scale both upwards and downwards, the correlation of the various physical phenomena and their mathematical expression in terms of which interpolations and extrapolations may be expresed, and in the invention and improvement of temperature measuring apparatus and methods.

The Thermodynamic Scale.—The fundamental basis for the determination of the temperature scale is obtained by measurements with some form of gas thermometer. The accuracy with which these and auxiliary measurements may now be made, together with the great purity now obtainable of the materials suitable for standard points, and the state of our knowledge of the gas laws, permits the expression of temperatures in terms of the *thermodynamic* or ideal-gas scale, a scale which is independent of the properties of any particular substance, and to which the usual gas scales approximate so closely that, for most purposes, it is not necessary to distinguish between them. The radiation laws, in terms of which extrapolation to the highest temperatures is made, are also based on the thermodynamic scale; so that, using this as our standard, we have a single temperature scale from the lowest to the highest temperatures. The corrections to apply to the scales given by gases, to reduce to the thermodynamic scale, are not yet known with all the certainty that may be desired especially at very low and very high temperatures, but in the former region the thermometric gases used, hydrogen and helium, depart less from the ideal state than any others, and in the case of helium the correction is practically negligible over almost the complete range of temperatures.

In the most recent researches in exact gas thermometry it is more and more the practice to reduce results to the thermodynamic scale, a practice that should become universal.

The Gas Scales.—The only methods of temperature measurement that are directly reducible to the thermodynamic scale are those based on the gas thermometers at constant pressure and constant volume, by means of computations based on the known properties of these gases.

Table I., based on recent computations, represents well enough the corrections to the gas scales in ordinary use and over the ranges within which these gases may be used to advantage. (See in particular computations by Callendar, *Phil. Mag.*, 1903, [6], v., 48; D. Berthelot, *Trav. et Mém. Bur. Inst.*, 1903, xiii.; Buckingham, *Bull. Bureau Standards*, 1907, iii., 237; Kammerlingh Onnes and Braak, "Seiden Coms." 1907, 97*b*, 102*b*; Rose Innes, *Phil. Mag.*, 1901, [6], ii., 130).

Within the fundamental interval, 0° to 100° C., the temperature scale has been defined by the International Committee on Weights and Measures in terms of hydrogen at constant volume under a pressure of 1000 mm. of mercury. This scale, as closely as it is known, appears to be practically identical with the thermodynamic scale. For lower temperatures the hydrogen and helium scales are used, the latter for the very lowest attainable, or to less than 1·2° K according to Kammerlingh Onnes. For high temperatures, especially above 450° C., nitrogen at constant pressure is usually used, although there is not here, nor for the range below 0° C., any international agreement as to the temperature scale. The upper limit attained is the melting-point of palladium, 1550° C. There is no necessity, at least from the point of view of the determina-

* Original communication, *Eighth International Congress of Applied Chemistry*, xxii., p. 53.

tion of temperatures, of extending gas thermometer measurements higher than this, as the thermodynamic scale is more nearly realised for those high regions by means of instruments based on the radiation laws the constants of which may be determined below 1550° C.

TABLE I.—*Scale Corrections for Gases*, $\theta_0 = 273{\cdot}10°$ C.

Temp. C.	Constant pressure=76 cm.			Constant volume, p_0=100 cm.		
	Helium.	Hydrogen.	Nitrogen.	Helium.	Hydrogen.	Nitrogen.
−250	—	—	—	+0·02	—	—
−200	+0·10	+0·26	—	+0·01	+0·06	—
−100	+0·03	+0·03	+0·33	0·000	+0·014	+0·07
−50	+0·009	+0·004	+0·09	0·000	+0·004	+0·02
+25	−0·002	−0·002	−0·013	0·000	0·000	−0·006
+50	−0·002	−0·003	−0·017	0·000	0·000	−0·006
+75	−0·002	−0·002	−0·012	0·000	0·000	−0·004
+150	+0·005	+0·003	+0·04	0·000	+0·001	+0·01
+200	+0·01	+0·01	+0·10	0·000	+0·002	+0·04
+450	+0·07	+0·04	+0·50	0·00	+0·01	+0·15
+1000	+0·24	+0·01	+1·7	—	+0·04	+0·70
+1500	—	—	+3·0	—	—	+1·3

Secondary Methods and Scales.—The most commonly used secondary temperature measuring instrument is the *mercury in glass thermometer*, the reductions of which to the hydrogen or thermodynamic scale, after all other corrections are made, depends on the kind of glass of which it is made, and to a much smaller extent on the history of the thermometer. The normal hydrogen scale is preserved at the International Bureau by means of four *verre dur* thermometers.

For high temperature thermometers—from 300° to 520° C. or more—the mercury is confined under pressure exerted by an inert gas, and if quartz is substituted for glass, 750° C. may be reached with mercury. For low temperatures the mercury may be replaced by toluene to −90°, and by pentane to liquid air temperatures.

All thermometers of the above types have to be calibrated empirically and individually in terms of known standards of temperature.

The Platinum Resistance Thermometer over the range in which it remains constant and sensitive, from −200° C. to +1000° C., and when properly designed, constructed, and used, is the most exact secondary instrument we have, and has been of great service recently in co-ordinating and comparing the gas thermometer observations on basal temperatures of several recent observers (Holborn and Henning, *Ann. d. Phys.*, 1911, xxxv., 761; Waidner and Burgess, *Bull. Bureau Standards*, 1910, vi., 149; vii., 1; Dickinson and Mueller, *Journ. Wash. Acad. Sci.*, 1912, ii., 176). For example, the lower freezing-point values, cadmium, zinc, &c., of Day and Sosman (*Am. Journ. Sci.*, 1910, xxix., 93; Reprint 157, Carnegie Institution of Washington, 1911), as well as boiling-points of naphthalene and benzophenone by Jaquerod and Wassmer (*Journ. Chim Phys.*, 1904, ii., 52), were shown definitely by the resistance thermometer measurements of Waidner and Burgess (*loc. cit.*) to be incompatible with the most probable value of the sulphur boiling-point (= S.B.P.), one of the most important of the base points, as it is commonly used with the freezing- and boiling-points of water, as the third calibration point of platinum resistance thermometers. The latest work on the sulphur boiling-point (Holborn and Henning, *loc. cit.*; Day and Sosman, *Am. Journ. Sci.*, 1912, xxxiii., 517; *Journ. Wash. Acad. Sci.*, 1912, ii., 167) with the constant volume gas thermometer has reduced the uncertainty of this temperature, which we may take as 444·6 on the thermodynamic scale, to less than 0·1° C., whereas a year ago this uncertainty was nearly 1·0 C.

The usual Callendar, or difference formula for reducing platinum temperatures $pt = 100\ (R\ R^0)/(R^{100} - R^0)$, to true temperatures, namely :—$t - pt = \delta(t/100 - 1)t/100$, where δ is a function of the purity of the platinum, has been shown recently to be of more general and exact application over a wider range of temperature than had hitherto been supposed (Adams and Johnston, *Am. Journ. Sci.*, 1912, xxxiii., 534; *Journ. Wash. Acad. Sci.*, 1912, ii., 275; Holborn and Henning, *loc. cit.*; Dickinson and Mueller, *loc. cit.*; Waidner and Burgess, *loc. cit.*). Using a base point within the fundamental interval, such as the transformation point of sodium sulphate, 32·383° (Richards and Wells, *Zeit. Phys. Chem.*, 1903, xliii., 465; Dickinson and Mueller, *Bull. Bureau Standards*, 1907, iii., 641) as the third calibration temperature, the value of δ for pure platinum is 1·470 to 1·480, and using the S.B.P., 444·6, the value of δ is 1·484 to 1·494. In other words, calibrating a platinum resistance thermometer in ice, steam, and sulphur vapour will give the normal International Hydrogen Scale, within the fundamental interval, 0° to 100°, to 0·004° C., or to closer than the International Bureau can reproduce its scale with certainty. In this range the platinum thermometer is reliable to better than 0·001° C. Using the platinum thermometer at high temperatures, or to 1100° C., in the same way with the Callendar formula, the temperature scale is reproduced as closely as this scale has been located by gas thermometer measurements, or to within 2° at 1100° C. It has been suggested to write the δ in the form $\delta \cdot \delta + at$. There appears to be no certain advantage of this more complex expression, however, for pure platinum.

For very low temperatures the Callendar formula breaks down, but to −200° C., it may be used with considerable exactness if the boiling-point of oxygen, −182·9, or the sublimation point of carbonic acid, −78·34°, is taken as the third calibration temperature. Complex exponential functions have also been suggested for very low temperatures, and resistances expressed in powers of temperature even to the fifth are sometimes used,

In precision calorimetry, the platinum thermometer replaces that of mercury to advantage, for when properly constructed the former has no appreciable zero change or hysteresis with use and time if not exposed to high temperatures, and it is as easy to measure small temperature differences at 25° C. to 0·0001° C. with the platinum as to 0·001 with the mercury thermometer. A great and unique practical advantage of the former for all uses above −100° C. is the fact that its calibration is made and controlled by only three fixed points which are easily realised with exactness, two of which are the ice and steam points, and the third *any* other known temperature which is most convenient.

The platinum thermometer becomes therefore the most satisfactory secondary standard for the calibration of all other types of thermometers between −200 and +1100° C. In fact, if the International Bureau were destroyed and all the existing copies of its thermometer standards as well, the International scale would be perpetuated with entire satisfaction by means of the platinum thermometer which may be constructed and calibrated independently anywhere it may be desired.

The Thermoelectric Thermometer, in general, is not an instrument of such great precision nor of such simple calibration as the platinum resistance thermometer, a formula involving three, and even four or more, powers of temperature in terms of E.M.F. being required for all thermocouples used with the highest accuracy over several hundred degrees, and at low temperatures over very much shorter ranges (Day and Sosman, *loc. cit.*, and Sosman, "Platinum Rhodium at High Temperatures," *Am. Journ. Sci.*, 1910, xxx., 1; Dickinson, Mueller, and White, "Copper Constants between 0—100," *Phys. Rev.*, 1910, xxxi., 159; Adams and Johnston, "Cu—Cu between 0 and 300," *loc. cit.*; J. Clay, "Couples at very Low Temperatures," Leiden Coms., 1908, 107*d*).

For temperatures below −200° C. a thermocouple of gold-silver appears to best meet the requirements of a secondary instrument (J. Clay, *loc. cit.*) For ordinary temperatures satisfactory couples are those of iron-constantan and copper-constantan; for high temperatures the Le Chatelier couple of Pt, 90 Pt-10 Rh.

For a moderate precision, the thermocouple is a most convenient instrument, and the calibration may then be reduced to three or even two reference temperatures. In the last case, for the Pt-Rh couple, the best formula appears to be Holman's, $\log e = a + b \log t$, for which, if the zinc and copper freezing-points are used as calibrating temperatures, the scale is off by less than 2·5° between 200° and 1300° C. and by less than 5° to the melting-point of platinum. For no form of thermocouple does it appear that the inverse function, which is the more convenient to work with, namely, $t = a + be + c e^2 + d e^3 + \ldots$, represents the temperature made with the same exactness as the form $e = a + bt + ct^2 + dt^3 \ldots$ with a like number of terms.

In Table II. are given the corrections to the readings of Pt, 90 Pt-10 Rh thermocouples calibrated at the freezing-points of zinc, antimony, and copper (see Table III.) for the usual three-term formula and in zinc and copper for the formula of two terms. The couples of Pt, 90 Pt-10 Ir have nearly the same corrections.

Table II.—*Corrections to Thermocouple Scales* (Pt, 90 Pt-10 Rh).

$t =$	$e = a + bt + ct^2$.	$\log e = a + bt$.
300	−0·8	−0·6
600	0	+1·5
900	+0·3	+2·5
1200	+0·5	−5
1400	+8	−5
1600	+26	−3
1700	+40	+1
1750	+46	+3

The inherent weakness, as compared with the platinum resistance thermometer, of any thermocouple as a secondary temperature standard is the impossibility of eliminating in the measurements the E.M.F. effects along the whole length of the wires between hot and cold junctions of the thermocouple, and no wire yet examined appears to be completely free from such effects of inhomogeneity.

For the estimation of very high temperatures we have the *radiation laws of Wien and of Stefan*, preference being given to the former based on the use of monochromatic light, mainly on account of experimental convenience, although the theoretical foundation of the second based on the use of total radiation is the more certain. The characteristic constants of neither of these laws are as yet determined in a wholly satisfactory manner, although considerable has been done in recent years on this subject, and work is still in progress.

We may take the value 14,500 for the characteristic constant c_2 in Wien's law $\log I/I_1 = c_2\lambda \log e\,(1/T_1 - I/T)$, in which I is the intensity of light of wave-length λ at an absolute temperature T. The recent determinations of c_2 all lie between 14,200 and 14,600. For the constant σ of Stefan's law connecting total radiation and temperature, $E = \sigma(T^4 - T_0^4)$, the value $\sigma = 5{\cdot}80$ watt. cm.$^{-2}$ deg.$^{-4}$ appears to be the most probable, although the range of recent determinations is 5·30 to 6·51.

Standard Temperatures.—Limiting ourselves to determinations made since the year 1900, and selecting only temperatures in the location of which two or more independent observers have participated, and which are suitable to use as check points in physical and chemical operations, the temperatures given in Table III. may be used as standard. They are given in terms of the thermodynamic scale, and for above 1550° C., the constant c_2 of Wien's law is taken as 14,500. Boiling-points are for a pressure of 760 mm. Hg, and are given only for substances that do not attack platinum, and for which it has been shown they remain constant over long periods of boiling.

As to the chemical purity of the various substances, Mylius has shown (*Zeit. Anorg. Chem.*, 1912, lxxiv., 407) that the following metals may easily be had to 0·01 per cent or better :—Au, Ag, Pt, Hg, Cu, Sn, Pb, Cd, Zn. Of the boiling substances, benzophenone and oxygen are the only ones to the purity of which special attention need be given. Due perhaps to the general practice of investigators working at very low temperatures to use the gas thermometer itself, instead of an auxiliary method, for measuring those temperatures, there is a dearth of exactly known fixed points in this part of the scale.

Table III.—*Standard Temperatures.—Thermodynamic Scale.*

Substance.	Phenomenon.	Temp. (°C.).	Uncertainty (°C.).	Reproducibility (°C.).
Hydrogen	Boiling	−252·7	0·2	0·05
Oxygen	Boiling	−182·9	0·1	0·03
Carbon dioxide	Sublimation in gasolene	−78·34	0·1	0·03
Mercury	Freezing	−37·7	0·1	0·05
Water	Freezing	0	0	0·001
$Na_2SO_4 + 10H_2O$.	Transformation to anhydrous salt	32·383	0·002	0·001
Water	Boiling	100	0	—
Naphthalene	Boiling	271·96	0·02	0·01
Tin	Freezing	231·85	0·1	0·05
Benzophenone	Boiling	305·90	0·05	0·02
Cadmium	Freezing	320·92	0·1	0·03
Lead	Freezing	327·4	0·1	0·05
Zinc	Freezing	491·4	0·1	0·15
Sulphur	Boiling	444·6	0·1	0·03
Antimony	Freezing	630	0·5	0·3
Ag_3—Cu_2	Eutectic freezing	779	1·0	1·0
NaCl	Freezing	800	2·0	1·0
Silver	Freezing	960·5	1·0	0·5
Gold	Freezing	1063	2·0	1·0
Copper	Freezing	1083	2·0	1·0
Palladium	Freezing	1549	10	3
Platinum	Melting	1755	15	5
Alumina	Melting	2000	30	20
Tungsten	Melting	3000	100	25
Carbon arc	Pos. crater	3600	150	50
Sun	Surface	6000	500	100

For the temperatures dependent on atmospheric pressures we have :—

Oxygen B.P. $T = T_{760} + 0{\cdot}013\,(p - 760)$

Carbon dioxide S.P. $T = T_{760} + 0{\cdot}017\,(p - 760)$

Water B.P. $T = T_{760} + 0{\cdot}037\,(p - 760)$

Naphthalene B.P. $T = T_{760} + 0{\cdot}058\,(p - 760)$

Benzophenone B.P. $T = T_{760} + 0{\cdot}063\,(p - 760)$

Sulphur B.P. $T = T_{760} + 0{\cdot}0912\,(p - 760) - 0{\cdot}000042\,(p - 760)^2$

(To be continued).

Royal Institution.—On Tuesday next, April 15th, at 3 o'clock, Prof. Wm. Bateson delivers the first of two lectures at the Royal Institution on "The Heredity of Sex and Some Cognate Problems," in continuation of those delivered before Easter. On Thursday, April 17th, Prof. J. Garstang begins a course of three lectures on "The Progress of Hittite Studies"; and on Saturday, April 19th, Prof. Sir Walter Raleigh commences a course of three lectures on (1) "Bocaccio," (2) "Mediæval French Novelists," (3) "Chaucer." The Friday Evening Discourse on April 18th will be delivered by Dr. T. M. Lowry on "Applications of Polarised Light"; and on April 25th by Prof. J. Garstang on "Meroë: Four Years' Excavations of the Ancient Ethiopian Capital" and on May 2nd by Mr. H. G. Plimmer on "Blood Parasites."

THE BEARING OF OSMOTIC PRESSURE ON THE DEVELOPMENT OF PHYSICAL OR GENERAL CHEMISTRY.*

By HARRY C. JONES,
The Johns Hopkins University, Baltimore, Md.

THE task that has been set me is an easy one. There is no other property of solutions which has played so prominent a rôle as osmotic pressure in the development of modern physical or general chemistry.

The young Dutch chemist van't Hoff was called at the age of twenty-four from Utrecht to Amsterdam to the chair of chemistry in the latter institution. Van't Hoff, even when a pupil with Kekulé in Bonn, was not content with the chemistry of his time. It did not appear to him to lead anywhere. To bring certain things together, to allow them to react chemically and then simply to determine the nature and properties of the products formed, did not appeal to him as sufficient, even if these steps were necessary to develop a branch of natural science. He wanted to know something about the nature of the reactions which gave rise to these products. He wanted to know at least the velocities with which these reactions take place, and the conditions which existed when equilibrium was reached. In a word, he wanted to know something about the dynamics of a chemical reaction.

While in this state of mind, and while pondering over the nature of chemical reactions, especially in solution, he met his colleague in the University of Amsterdam, Hugo DeVries, then botanist there, a man who has since become very famous, as is well known to this company. DeVries thought that van't Hoff might obtain some aid in solving the problems that he had in mind from the work of Pfeffer on the osmotic pressure of solutions of cane-sugar and a few other substances, which, as is well known, was published as a monograph in 1877 under the title "Osmotische Untersuchungen."

This was the introduction of van't Hoff to the work of Pfeffer, and this introduction marks an epoch in the development of the science of chemistry. Let us now see why.

Pfeffer had measured the osmotic pressure of certain solutions of cane-sugar and a few other compounds, to learn the order of magnitude of this force. He had gone at the problem as a plant physiologist would do, and had solved it from this standpoint. He measured more accurately than any one else had done the magnitude of osmotic pressure, and this was his aim. Where Pfeffer left this problem was where van't Hoff took it up.

Van't Hoff first observed from Pfeffer's data that there is a very simple relation between osmotic pressure and the concentration of the solution exerting it. This can be seen from the following data:—

Percentage concentration of cane-sugar (C). Per cent.	Osmotic pressure (P). Cm.	P/C.
1	53·5	53·5
2	101·6	50·8
4	208·2	52·0
6	307·5	51·2

It will be observed that P/C is a constant, which means that osmotic pressure is proportional to the concentration of the solution. This is in itself not surprising. To say that the osmotic pressure of a solution is proportional to the concentration of the solution, is simply to say that two molecules in solution exert just twice the osmotic pressure of one molecule, and there are many similar properties of substances—the one being a linear function of the other.

To an average mind this would mean nothing more than that the one property of the dissolved substance was proportional to the other. But van't Hoff's mind was not of the average type. Indeed, very far from it. In looking over the history of chemistry I can find no name which stands for more in the development of scientific chemistry than J. H. van't Hoff. Indeed, it is a question in my mind whether anyone else has contributed quite so much in so many different directions. Van't Hoff is not only one of the very greatest chemists of all time, but one of the greatest men of science of his century. It is well known that he died at the early age of fifty-nine in Berlin, somewhat more than a year ago.

In the ratio P/C equals a constant, van't Hoff saw an analogy to the law of Boyle for gases. This law is usually stated that the pressure times the volume of a gas is a constant. But since the concentration of a gas, or the number of parts in a given space, varies inversely as the volume, we can say that the pressure of a gas divided by the concentration is a constant. In a word, the pressure of a gas varies as the concentration.

These two properties, the pressure of a gas and the osmotic pressure of a solution, might both obey Boyle's law as they do, and yet have nothing very fundamental in common. There are many properties of substances in nature which vary the one with the other.

Van't Hoff went further than this. If there is any real relation between solutions and gases, then other laws of gas pressure must apply to the osmotic pressure of solutions. Let us see whether this is true.

Another well-known law of gas pressure is that of Gay-Lussac. This states that the pressure of a gas increases 1/273 for every rise in temperature of 1° C. the volume being kept constant. This raises the question, does osmotic pressure increase with rise in temperature and if so, how much? The measurements of Pfeffer enable us to answer this question. He not only measured the osmotic pressure of solutions of cane-sugar at different concentrations, but the osmotic pressure of a given solution of cane sugar at different temperatures.

The temperature coefficient of osmotic pressure as calculated from Pfeffer's work is approximately 1/273; but this is only an approximation; there being comparatively wide deviations in the results obtained by Pfeffer bearing on this question.

Fortunately there is an indirect method of testing whether the law of Gay Lussac applies to the osmotic pressure of solutions. This method is based upon a principle discovered by Soret. When all of the different parts of a homogeneous solution are maintained at the same temperature, the whole solution will remain of homogeneous concentration; that is, all the different parts will have the same concentration.

If, however, one part of the solution is heated to a different temperature from the remainder, the warmer part becomes more dilute and the colder part more concentrated. This is known as the principle of Soret.

If Gay-Lussac's law applies to the osmotic pressure of solutions, then since, as we shall see, osmotic pressure is the cause of all diffusion, we should be able to calculate the difference in concentration of different parts of a solution heated to different temperatures, from the difference in temperature of the different parts of the solution in question.

A moment's reflection will show this to be true. The warmer solution becomes more dilute because the osmotic pressure of a warm particle is greater than that of a cold particle. This excess of osmotic pressure drives the dissolved substance over from the region of greater pressure to the region of lesser pressure, from the warmer to the colder part of the solution—and this continues until there is an equality of osmotic pressure in all parts of the solu-

* At the Clevedon meeting of the Botanical Society of America a symposium on Permeability and Osmotic Pressure was held, in which the following subjects were discussed:—
I. "Osmotic Pressure and Semi-Permeability in Animal Cells," by Jacques Loeb.
II. "The Bearing of Osmotic Pressure on the Development of Physical or General Chemistry," by Harry C. Jones.
III. "Quantitative Researches on the Permeability of Plant Cells," by W. J. V. Osterout.
IV. "Osmotic Pressure and Related Forces as Environmental Factors," by Burton E. Livingston.

tion. If the difference in temperature of the two parts of the solution is, say 50°, then the colder solution should be 50/273 more concentrated than the warmer. The results of experiment agree so closely with the result of calculation that we can say that osmotic pressure and gas pressure have the same temperature coefficients, or, in other words, the law of Gay-Lussac applies to the osmotic pressure of solutions.

The third law of gas pressure that we wish to consider is the law of Avogadro. This says that those gases which contain the same number of parts or molecules in a given volume have the same gas pressure. It is very easy to test this law for osmotic pressure, and van 't Hoff did so in the following way. He took hydrogen gas of a certain definite concentration, that is, containing a certain number of molecules in a given volume, and calculated its gas pressure. He then took a solution of cane-sugar containing the same number of molecules dissolved in a given volume of the solvent that there were molecules of hydrogen in the same volume of space. He compared the osmotic pressure of the solution of cane-sugar with the gas pressure of the hydrogen gas, and found that the true pressures were *exactly equal. This was a most remarkable discovery.* That the gas pressure exerted by a gas particle should be exactly equal to the osmotic pressure of a dissolved particle under the same conditions of concentration, could never have been suspected until it was demonstrated experimentally.

Let me make a slight digression here to avoid confusion. Gas pressure and osmotic pressure are identical in result, that is in their magnitude. But this does not say that they have identical or even closely related causes. As we shall see, we do not to-day, in my opinion, know the cause of osmotic pressure, while we have a very satisfactory theory to account for gas pressure. The kinetic theory of gases tells us that the cause of gas pressure is the bombardment of the walls of the confining vessel by the rapidly moving gas particles. It is difficult, not to say impossible, to account for osmotic pressure on the basis of any such dynamical theory. We know that dissolved particles move through the solvent with very small velocities, with velocities altogether too small to give us osmotic pressure in any manner analogous to that with which gases produce pressure on the walls of the vessels that contain them. Let us, therefore, be very careful to distinguish between the fact that gas pressure and osmotic pressure under comparable conditions are equal, and what we might imagine to be true, but which has not the slightest foundation in fact, viz., that gas pressure and osmotic pressure have a common cause.

The three most fundamental laws of gas pressure, then, apply to the osmotic pressure of solutions. But of what importance is this generalisation or the discovery of such relations?

Let us leave this question for a moment, until we have looked a little more closely and thoroughly into the properties of solutions in general. That the laws of gas pressure apply to the osmotic pressure of solutions of substances such as cane-sugar is obvious from what has been said. But this is not the whole truth. Solutions of acids, bases, and salts exert osmotic pressures that are too great in terms of the gas laws. But acids, bases, and salts are those substances which, when dissolved in water, conduct the electric current. These are the electrolytes, while cane-sugar is a typical non-electrolyte. Electrolytes, then, in general have osmotic pressures that do not obey the laws of gas pressure, but are too great in terms of these laws. What does this mean?

The answer to this question is the theory of electrolytic dissociation proposed in 1887 by Arrhenius, and the paper announcing this theory was published in the same volume of the *Zeitschrift fur Physikalische Chemie* (vol. i.) as van 't Hoff's paper on the relations between gas pressure and osmotic pressure.

¶The theory of electrolytic dissociation, as is well known, states that acids, bases, and salts, when dissolved in a dissociating solvent like water, break down into charged parts or ions, and that it is these parts which are the active agents chemically. The evidence for the general correctness of this theory comes from so many independent sources, and is now so overwhelming, that I know of no productive chemist who fails to accept it at least as a basis of work.

It would lead us too far here, and it would be quite superfluous, to attempt to present even a few of the many lines of evidence bearing on this theory, in the brief time at my disposal. Suffice it to say that this theory when taken with the relations between gas pressure and osmotic pressure gave us the first scientific theory of dilute solutions.

Importance of a Correct Theory of Solutions.

This raises our old question, of what scientific value is a correct theory of solutions? I wish to dwell a little upon this point on account of its fundamental importance. Van 't Hoff showed that the laws of gas pressure apply to the osmotic pressure of solutions. In a word, there is some close connection between the properties of solutions and those of gases. Why was this step so distinctly epoch-making?

We know matter in three stages of aggregation, solid, liquid, and gas. Of the first we know comparatively little. We are familiar with the crystallographic forms and the systems in which matter crystallises. We pass different forms of energy; heat, light, electricity, &c., through matter in the solid state, and observe its conductivity for energy, as it is termed. But after all we know very little about solids. We do not know even the chemical formula of ice or rock-salt. The one we say is H_2O, but we know that this is not true. We know that it is $(H_2O)x$, but we do not know the value of x, and have no reliable means at present of finding it out. We write rock-salt NaCl, but we know that it is $(NaCl)y$, and the y in this case is just as much of an enigma as the x in the case of water. I cite these cases to illustrate how nearly perfect our ignorance of matter in the solid state is, even at present. We know practically nothing about the laws of solids.

When we come to liquids our knowledge is only a little more satisfactory. We do know more about liquids than about solids. We know in many cases their molcular aggregation or, as we say, their molecular weights. We have studied many of their physical properties. But with this state of aggregation of matter our knowledge is not only far from complete but, indeed, very unsatisfactory. We know very little about the laws to which matter in the liquid condition conforms.

When we come to gases it is fortunately a different story. Here we actually know a great deal. Many of the fundamental problems of gases may to-day be said to be solved. We know the laws of gas pressure. We know the molecular weights of substances in the gaseous state, and this is fundamental to the determination of the atomic weights of the various chemical atoms. We know a good deal about the inner mechanism of gases when conducting heat, light, and electricity, due especially to the recent beautiful investigations of Sir J. J. Thomson. We can deal with gases by thermodynamical methods and apply the first and second principles of this, an exact mathematical science, to them. All in all, we know infinitely more about matter in the gaseous state than in the liquid and solid states both taken together.

We can now see why it is so important to be able to deal with solutions as we can deal with gases. We are thus able to deal with solutions to some extent by the rigid mathematical methods to which gases conform. Since the discovery made by van 't Hoff we really know something about matter in solution, but this raises the further question why is it so important to deal with solutions by the exact scientific method, or by any method whatsoever? Why is a knowledge of solutions so fundamental not only for chemistry, but for so many of the other branches of

natural science? And this question brings us to the most important part of our task.

The Importance of Solutions.

A moment's reflection will show the importance of solutions for natural science in general. The term solution is used here in the broadest aspect of the subject. We know matter in three states of aggregation, solid, liquid, and gas. A solution is a homogeneous mixture of matter in the given state of aggregation with matter in the same or a different state of aggregation, the component parts of which cannot be separated mechanically. In terms of this definition we can have solid, liquid, or gas acting as a solvent, and every state of aggregation dissolved in its own or in any other state of aggregation. We would, consequently, have nine types of solution.

Bearing in mind this broader definition of solution, the meaning of what follows should be clear. The whole science of chemistry is only a branch of the science of solutions. Think of all the chemical reactions you can, and see how many do not take place in solutions in the broader sense of the term. Of course, all reactions that take place at high temperatures between fused masses are reactions in solution, because the term solution does not raise any question as to temperature.

You will find that the number of chemical reactions that take place outside of solution is extremely small, and it is thus obvious that solution is a fundamental condition for all chemistry.

But let us turn to geology. The rocks are either precipitated from aqueous solutions or aqueous suspensions, colloidal or otherwise, or crystallised from molten magmas —and the latter are as true solutions as the former; the difference being chiefly a difference in temperature. Thus, solutions underlie geology.

Take the biological sciences. Physiology, both vegetable and animal, what would it be without matter in the dissolved state? Without solution of course no life. We often say without carbon no life, but it is just as true that without solution we could not have living matter persist for any long period of time and reproduce itself. Take pharmacology, therapeutics, and indeed the whole science of medicine, where would they be without solutions? The reason that processes go on in living matter in solution is probably closely connected with the fact that chemical processes in general take place entirely or very nearly so in solution, in the broad sense in which we are using the term.

The above would suffice to show the importance of matter mixed with other matter, of solution, for the natural sciences in general. If solutions did not exist the whole face of nature would be changed. There would be no chemistry, consequently, no biology, and no geology. It is appalling, not to say impossible, to think of what nature would be were it not for the properties of matter in the dissolved condition. It is only when we bring matter into the presence of some other kind of matter—into solution —that it becomes active from the chemical, biological, and geological standpoints; and these various sciences owe their existence to matter in the dissolved state.

It is thus obvious that if we are ever to have a really exact science of chemistry, geology, or biology, even as we have a science of physics to-day, we must first know the condition and properties of matter in that state which gives us these sciences.

The importance of the generalisations of van't Hoff and Arrhenius as to the nature of solution and the relations between solutions and gases for the development of a real science of chemistry, in contradistinction to a heterogeneous mass of more or less disconnected facts, cannot easily be overestimated.

The announcement of these generalisations in 1887 marked a new epoch in the history of chemistry, and the beginning of what we may fairly call a real science of chemistry. From 1887 to the present, general chemistry has made more progress towards becoming a branch of really exact science than in the entire century which elapsed prior to 1887; and these generalisations as to the nature of solutions came as the result of van't Hoff comparing Pfeffer's measurements of osmotic pressure with the gas pressure of gases. This alone would suffice to show the fundamental significance of osmotic pressure for the development of general chemistry.

In making the above statement in reference to the enormous strides that scientific chemistry has taken since 1887, I am not unmindful of the fact that the law of mass action was discovered and its discovery published in 1868, but the law of mass action without the work herein discussed on the nature of solution was comparatively barren. Indeed, it was this same van't Hoff who first applied successfully the law of mass action to chemical reactions, and this, after he had shown the inherent relation between solutions and gases.

It is not quite fair to leave the subject of the bearing of osmotic pressure on the theory of solutions, without saying a few words at least with reference to concentrated solutions, especially of electrolytes.

The theory of Arrhenius, which it will be remembered was proposed to account for the abnormally great osmotic pressure of electrolytes, was really a theory of "ideal" or "very dilute" solutions. It not only did not apply to concentrated solutions, but not even to those concentrations with which we actually work in the laboratory—not to those solutions which give us chemistry, biology, &c. Such solutions were in general found to exert osmotic pressures that are too great even if we take into account the dissociation of such solutions. And here again there was for a time considerable trouble. We had a theory of solution which might be called a theory of ideal conditions which were of very little use in science—a theory which did not apply to the very cases in which men of science were most interested.

We think that we have now a fairly satisfactory explanation of the apparently abnormal results presented by solutions of moderate and of great concentration. The solvate theory of solution says that a dissolved substance combines with more or less of the solvent, and this theory must be regarded merely as supplementing the theory of electrolytic dissociation. The dissolved substances combining with more or less of the solvent remove it from the field as part of the solvent. These solutions are concentrated by just so much solvent as is combined with the dissolved substances, and are in reality more concentrated than we would suppose them to be from the amount of substance dissolved in them. This conclusion seems to be justified by the work of this and other laboratories during the past fifteen years. Indeed, more than a dozen independent lines of experimental evidence all pointing to the correctness of the solvate theory of solutions have been brought to light in this laboratory alone during the past ten years.

Without going into any detail here on this point, suffice it to say that when the theory of electrolytic dissociation is supplemented by the solvate theory of solution, which enables us to calculate the amount of solvent combined with the dissolved substance—to calculate the true concentration of the solution—we can then calculate the osmotic pressure of fairly concentrated solutions approximately, knowing the amount of their dissociation. In a word, we have to-day a theory of the nature of the real solutions that we use in biology and in chemistry, and we have already seen the meaning of such a theory for the biological sciences in general.

Osmotic Pressure and Diffusion.

In concluding let me say a few words with reference to the bearing of osmotic pressure on general chemistry from a somewhat different standpoint. There is no property of solutions with which we are more familiar than with diffusion. Whenever a solution of one concentration is brought in contact with a solution of a different concentration, we have the dissolved substance passing over from

the region of greater to the region of lesser concentration, and this continues until homogeneity is established in all parts of the solution, provided the temperature of all parts of the solution is kept the same.

We are so familiar with this phenomenon that we are liable not to stop and ask any questions concerning it. Yet a moment's thought will show that we are dealing here with a very remarkable phenomenon. Take a cylinder of water of almost any reasonable height, and place on the bottom of that cylinder some very heavy soluble substance, say lead nitrate, mercuric chloride, or platinic chloride. This heavy substance will dissolve and will rise through the comparatively light water up to the top of the cylinder.

This phenomenon differs in degree, but somewhat resembles the phenomenon that would be presented by our rising directly through the atmospheric air, although we are a great many times heavier than the air.

We cannot study the phenomenon of diffusion without recognising that we have some very powerful force at work, driving the heavy dissolved substance upwards against the pull of gravity through the much lighter solvent, and we must ask what is the nature of this force.

A quantitative study of the phenomena of diffusion shows that they obey the laws of osmotic pressure. Fick's law for diffusion states that the amount of dissolved substance that will pass through a given cross section separating two solutions of different concentration, is proportional to the difference in concentration on the two sides of that section. This will be recognised at once as nothing else than Boyle's law for gases, which states that the pressure exerted between two gases brought in contact is proportional to the difference in concentration of the two gases. We have seen that the osmotic pressure of solutions obeys the law of Boyle for gases, and we now learn that diffusion obeys this same law. This is, then, one analogy between the phenomena of osmotic pressure and those of diffusion.

We have already become familiar with the beautiful principle of Soret, which shows that the temperature coefficient of diffusion is the same as that of a gas. In other words, temperature has the same effect upon diffusion that it has upon gases, and the law of Gay-Lussac applies to both phenomena. The law of Gay-Lussac, as we now know, also applies to osmotic pressure, and this is a second analogy between osmotic pressure and diffusion.

By comparing the phenomena of diffusion in general with those of osmotic pressure in the broadest possible way, we learn that we are justified in concluding that the two sets of phenomena obey throughout the same laws, and we conclude that osmotic pressure is the cause of all diffusion.

Osmotic pressure is then the force which drives the heavy dissolved substance through the solvent even against the pull of gravity until the whole system becomes homogeneous. It is capable, as we have seen, of driving a very heavy substance up through a light solvent to a very great height, and of establishing and maintaining equilibrium of concentration in solution.

Let us now think for a moment what diffusion really means for general chemistry. If it were not for diffusion, therefore, if it were not for osmotic pressure, it would be impossible to maintain the different parts of the solution at the same concentration for any appreciable period of time. Indeed, this condition in solution could be secured only approximately by keeping the solution in question in most violent agitation. If a solution would not maintain itself homogeneous, it would be a most serious matter not only for quantitative chemistry, but for quantitative work in any branch of the biological sciences in which solutions are used, and most of them employ solutions in one way or another. It would be especially serious for the recent developments in botany and zoology, which have come about by varying the conditions to which the organism is subjected and observing what changes are produced in it. Without the property which solutions have of remaining homogeneous or standard, all volumetric methods in chemistry would be wiped out and experimental biology could not have hoped to achieve what has already been done, or to advance as rapidly as we may reasonably expect it to do in the near future.

Perhaps this brief sketch may serve to give some faint conception of the importance of osmotic pressure as a property of solutions, especially in maintaining solutions homogeneous for the development, from the quantitative side, of not only chemistry but many other branches of natural science.

And, again, consider the osmotic pressure of colloids or colloidal solutions. This whole subject has come very much to the front in the last few years, in connection with the tremendous developments in the field of colloidal chemistry. We all well remember that it was only a few years ago that colloids were suspected of having no osmotic pressure, and yet in many so-called colloidal solutions we had phenomena manifesting themselves that were at least analogous to diffusion; and how can we have diffusion without osmotic pressure when the latter is the cause of the former?

More recent work indicates that these colloidal solutions, and perhaps some of the colloidal suspensions in which the parts are much larger than in colloidal solutions, actually have osmotic pressure, and it would not be surprising if it should ultimately be shown that the osmotic pressure of colloidal solutions obeys the same general laws as the osmotic pressure of so-called true solutions. In colloidal solutions we know that matter is much less finely divided than in true solutions, and, consequently, the number of physical units present for any given amount of substance in suspension is much smaller in the colloidal than in the dissolved state. It is, therefore, not surprising that such colloids should, in the presence of say water as a solvent, exert much smaller osmotic pressure than equivalent concentrations of crystalloids, in which we know the parts in the presence of the solvent are in a much finer state of subdivision. The rôle of osmotic pressure, and of surface tension, which is probably very closely connected with it, will, in my opinion, be very prominent in the future development of colloidal chemistry, from which much is to be expected.

Then take the application of osmotic pressure to the action of the primary cell, about which I must say only a word. The primary cell was discovered by Volta more than a hundred years ago, and its action was not understood until the present theory of solutions was worked out by van 't Hoff and Arrhenius. Knowing the osmotic pressure of the solutions around the two electrodes in the primary cell, we are not only able to calculate the electromotive force of such cells, but are able to explain satisfactorily the action of all the simpler forms of primary cells. The bearing of osmotic pressure, then, upon this fundamental chapter of electrochemistry is obvious and most important.

I should not close what I have to say in reference to osmotic pressure without adding a few words concerning the magnificent measurements of osmotic pressure which have been, and are being made by my colleague, Prof. H. N. Morse and his co-workers. They have not only made the most accurate measurements of osmotic pressure, but in doing this have overcome difficulties which to any less skilful investigators would have been considered as absolutely insurmountable. We now know the osmotic pressures of cane-sugar with accuracy certainly to the second decimal, and over a very wide range in temperature. This work is undoubtedly to be placed among the classics in science for the difficulties met and overcome, and for the accuracy of the measurements that are now being made.

Just one word more in reference to the nature of osmotic pressure. What is osmotic pressure? Or what causes it? I do not know nor do I believe that anyone else at present does. The number of attempted explanations of what osmotic pressure is or what

causes osmotic pressure is literally legion. It seems to me that nearly everyone who has not anything better to do, or who wishes to write a paper for which a suitable subject has not been selected, favours us with his opinions as to what the nature of osmotic pressure really is.

As the result of reading more of these papers in the past than I shall do in the future, I have come to the above conclusion, which, frankly expressed, is that we do not know and at present have no means of finding out what really causes osmotic pressure. It seems probable from the splendid work of Morse, that when osmotic pressure is explained we will have to take into account the fact that the colloidal semi-permeable membrane used in measuring it, probably takes up water from the outside and becomes hydrated, and that the solution in some unknown way dehydrates this membrane on the inside. But after all this is not very much more than words.

What we do know, and in my judgment about all that we do know at present in reference to the nature of osmotic pressure, is that it is in some entirely unknown way connected with the surface-tension of the solutions between which it manifests itself. Whenever we have a satisfactory theory of osmotic pressure, it seems highly probable that that theory must take into account the phenomena which manifest themselves in capillary tubes, which we call surface-tension, and this probably exerts itself in the fine capillaries in the semipermeable membranes.

Although we do not to-day know the cause of osmotic pressure yet we know its result. Its magnitude has now been accurately measured and its significance in connection with solutions pointed out by van't Hoff and Arrhenius.

I hope some idea as to the importance of osmotic pressure in the development of general chemistry may be gained from what has already been said. All in all, it is to be regarded as the most important property possessed by matter in the dissolved state.—*The Plant World*, xvi., 73.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, March 6th, 1913.

Prof. PERCY F. FRANKLAND. LL.D., F.R.S.. President, in the Chair.

(Concluded from p. 165).

63. "*Perezone.*" By FREDERIC GEORGE PERCY REMPFRY.

The hydroxy-quinone perezone (pipitzahoic acid, $C_{15}H_{20}O_3$, is converted by the action of heat into a colourless isomeride melting at 140—141° (corr.), and having $[\alpha]_D$ +13·1°, which has been termed *perezol*. This substance is phenolic, and yields a monoacetyl derivative, *acetyl perezol*, melting at 114—115° (corr.), and having $[\alpha]_D$ +6·2°. The latter is identical with the colourless compound obtained by Anschütz and Leather (*Annalen*, 1887, ccxxxvii., 90) by the action of acetic anhydride on perezone.

Perezol and acetylperezol are, further, doubtless identical with the substances prepared by Sanders (*Proc.*, 1906, xxii., 134), to which, however, different formulæ were assigned.

Perezone yields *alkylquinoles* when treated with magnesium alkyl iodides.

By-products produced in the preparation of hydroxyperezone and perezinone have also been studied.

64. "*Polybromides in Nitrobenzene Solution.*" By ALFRED FRANCIS JOSEPH.

The solubility of potassium bromide in nitrobenzene solutions of bromine has been measured, and from the results the existence of a polybromide, KBr_{2n+1}, may be inferred, for which n is about 1.

The rate of molecular concentration of bromine to molecular solubility of bromide increases from 1·87 to 3·11 as the former increases from 0·075 to 1·5, but it was shown that this does not indicate the presence of polybromides, for which n is greater than 1.

The colorimetric study of the solutions leads to the same conclusion.

65. "*Action of αγ-Dibromobutane on the Sodium Derivatives of Ethyl Acetoacetate and Benzoylacetate.*" By ROBERT GEORGE FARGHER and WILLIAM HENRY PERKIN, jun.

αγ-Dibromobutane reacts readily with the sodium derivative of ethyl acetoacetate with the formation of *ethyl* 2 : 6-*dimethyl* 2 : 3-*dihydro*-1 : 4-*pyran*-5-*carboxylate*,

$$O<\begin{matrix}CMe{:}C(CO_2Et)\\ CHMe\text{——}CH_2\end{matrix}>CH_2,$$

which melts at 35° and distils at 225—226°/750 mm. The corresponding acid melts at 126°, and is decomposed on distillation into 2 : 6-*dimethyl*-2 : 3-*dihydro*-1 : 4-*pyran*, a mobile oil distilling at 120°. When the acid is boiled with water it loses carbon dioxide, and the dihydropyrane ring suffers hydrolysis with formation of *heptan*-ζ*ol*-β-*one*, $CH_3{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_3$, a viscid syrup, which distils at 117°/20 mm., and is converted by oxidation with chromic acid into *heptane*-βζ-*dione*, $CH_3{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}CH_3$, which melts at about 31°, and distils at 202°/754 mm. Reduction with sodium amalgam converts heptan ζ-ol β-one into *heptane*-βζ-*diol*, which distils at 140°/50 mm., and, when heated under the ordinary pressure, is gradually decomposed with the formation of 2 : 6-*dimethyl*-2 : 3 :5:6-*tetrahydro*-1 : 4-*pyran*—

$$O<\begin{matrix}CHMe{\cdot}CH_2\\ CHMe{\cdot}CH_2\end{matrix}>CH_2,$$

a mobile oil distilling at 118°/756 mm.

βζ-*Dibromoheptane*, $CH_3{\cdot}CHBr{\cdot}[CH_2]_3{\cdot}CHBr{\cdot}CH_3$ (b. p. 100°/12 mm.), is obtained when heptane-βζ-diol is digested with phosphorus tribromide.

ζ-*Bromoheptan*-β-*one*, $CH_3{\cdot}CO{\cdot}[CH_2]_3{\cdot}CHBr{\cdot}CH_3$, produced by the action of concentrated hydrobromic acid on ethyl dimethyldihydropyrancarboxylate, distils at 130°/50 mm.

When the sodium derivative of ethyl benzoylacetate is digested with αγ-dibromobutane, *ethyl* 6-*phenyl*-2-*methyl*-2 : 3-*dihydro*-1 : 4-*pyran*-5-*carboxylate*, is obtained as a colourless crystalline mass, melting at 58°. 6-*Phenyl*-2-*methyl*-2 : 3-*dihydro*-1 : 4-*pyran*-5-*carboxylic acid*—

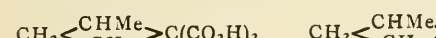
$$O<\begin{matrix}CPh{:}C(CO_2H)\\ ChMe\text{——}CH_2\end{matrix}>CH_2,$$

melts at 147°, and is decomposed on heating with elimination of carbon dioxide and formation of 6-*phenyl*-2-*methyl*-2 : 3-*dihydropyran* (b. p. 251°/758 mm.), and, when boiled with water, the acid yields α-*phenyl*-*hexan*-ε-*ol*-α-*one*, $C_6H_5{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_3$, which melts at 34°, and is reduced by sodium amalgam to *phenyl*-*hexane*-αε-*diol*, which is a syrup. Careful oxidation with chromic acid converts phenylhexanol into α-*phenylhexane*-αε-*dione*, $C_6H_5{\cdot}CO{\cdot}[CH_2]_3{\cdot}CO{\cdot}CH_3$, a crystalline substance, which melts at 65°. *Phenyl* ε-*bromo*-α-*phenyl*-*hexan*-α-*one*, $C_6H_5{\cdot}CO{\cdot}[CH_2]_3{\cdot}CHBr.CH_3$, is obtained, when ethyl phenylmethyldihydropyrancarboxylate is left in contact with concentrated hydrobromic acid, as a syrup which distils with much decomposition at about 188°/21 mm.

66. "*Action of αγ-Dibromobutane on the Sodium Derivative of Ethyl Malonate.*" By GIBBS BLACKSTOCK and WILLIAM HENRY PERKIN, jun.

This interaction leads to the formation of a number of substances, one of which is *ethyl* 1-*methylcyclobutane*-2 : 2-*dicarboxylate*. This ester, on hydrolysis, yields

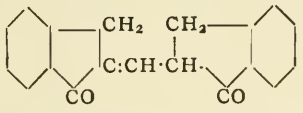
1-*methyl*cyclo*butane*-2 : 2-*dicarboxylic acid* (I.), which crystallises from dilute hydrochloric acid in prisms, and melts at 160—162°. This dibasic acid is decomposed on distillation, with elimination of carbon dioxide and formation of 1-*methyl*cyclo*butane*-2 *carboxylic acid* (II.), which is an unpleasant smelling oil distilling at 198°/755 mm. The authors are engaged on the resolution of this acid into its active constituents, and also on the examination of the other substances produced in the above interaction.



I. II.

67. "*Studies on Cyclic Ketones.*" Part III. By Siegfried Ruhemann and Stanley Isaac Levy.

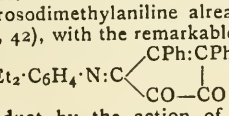
The constitution of the red condensation product,—



previously obtained by the action of heat on 2-hydroxymethylene-1-hydrindone (*Trans.*, 1912, ci., 2549) has been verified by the study of its behaviour towards bromine. Experiments have now been made with the object of preparing similar substances from diphenyl*cyclo*pentenone and from β-hydrindone, but these attempts were unsuccessful, as no hydroxymethylene derivatives of these ketones could be obtained.

These experiments, in turn, led to the investigation of the action of aromatic aldehydes on the two ketones. It was found that, under the influence of hydrogen chloride, condensation readily occurs with 2 molecules of the aldehyde. With *o*-hydroxyaldehydes the reaction proceeds one stage further, polycyclic *spiro*pyran compounds being formed. Substances of this nature have been obtained from both ketones by the action of salicylaldehyde and of 1-aldehydo-2-naphthol ; they are characterised by the deep colour and strong fluorescence of their solutions in concentrated sulphuric acid.

The action of *p*-nitrosodiethylaniline on diphenyl*cyclo*pentenone is found to be exactly parallel to the reaction with nitrosodimethylaniline already investigated (*Trans.*, 1912, ci., 42), with the remarkable difference that the compound



, which is formed from the product by the action of hydrochloric acid, does not possess the property of forming colloidal solutions, which characterises the analogous derivative obtained from *p*-nitrosodimethylaniline.

68. "*The Interaction of Chlorine and Hydrogen. The Influence of Mass.*" By David Leonard Chapman and Leo Kingsley Underhill.

The authors have determined the sensitiveness to light of mixtures containing chlorine, oxygen, and hydrogen, the object having been to find the variation of the rate of formation of hydrogen chloride when the concentration of the chlorine and oxygen were kept constant, and that of the hydrogen varied. The concentration of the oxygen was small in comparison with that of the chlorine. It was found that as the concentration of the hydrogen was increased from zero, the sensitiveness increased at first very rapidly, attained a maximum value, and then gradually fell. Thus, a mixture which contained 50 per cent of hydrogen was only twice as sensitive as one which contained only 3 per cent, whilst the sensitiveness of a mixture containing 100 per cent of hydrogen was less than that of a mixture containing 50 per cent in the ratio of 7 to 10.

The above results demonstrate conclusively that the rate of formation of hydrogen chloride is not under ordinary conditions proportional to the number of impacts per second between pairs of molecules of hydrogen and chlorine. Accordingly the conclusion of Wilderman (*Phil. Trans.*, 1902, cxcix., 337), that the rate of interaction of chlorine and carbon monoxide is proportional to the concentration of the colourless constituent is not true for the closely analogous chemical action between chlorine and hydrogen. Even if true therefore for the special case investigated by Wilderman, his conclusion cannot be regarded as generally applicable to photochemical changes.

The results of the authors are in agreement with the view that by the action of light a comparatively unstable form of chlorine is produced, and that this, in the presence of a sufficient quantity of hydrogen, is almost entirely converted into hydrogen chloride, whereas in the presence of a deficiency of hydrogen it reverts largely to ordinary chlorine.

69. "*The Behaviour of Calcium and Magnesium Salts with Soap Solutions, and the Determination of Hardness of Water.*" By Helen Masters and Henry Llewellyn Smith.

It is well known that in the titration of hard waters with soap solution equivalent amounts of calcium and magnesium salts use up different quantities of soap, magnesium salts using up more than calcium salts.

It is the unsaturated acids that cause this difference, saturated fatty acids giving soap solutions, which give accurate results with calcium salts and magnesium salts or with mixtures of the two.

Potassium myristate makes a convenient stable solution for this purpose.

The solubility of calcium oleate decreases, whilst the solubility of magnesium oleate increases with rise of temperature.

With magnesium salts and sodium oleate a precipitate soon forms after titration at 15°, and this carries down or adsorbs some sodium oleate, and no more soap is required. With calcium salts and sodium oleate at 15° no precipitate forms under the usual conditions, the liquid remaining translucent.

With soaps made from the saturated fatty acids precipitates form with both calcium and magnesium salts.

70. "*Organic Derivatives of Bismuth.*" (Preliminary Note). By Frederick Challenger.

With the object of preparing organic compounds of bismuth possessing an asymmetric structcre, and the resolution of which into optically active components might, under suitable conditions, conceivably be accomplished, the preparation and properties of certain organic derivatives of bismuth are being studied.

Pfeiffer and Pietsch (*Ber.*, 1904, xxxvii., 4620) showed that bismuth chloride reacts with an ethereal solution of magnesium phenyl bromide with the formation of triphenylbismuthine in a 25 per cent yield. This compound was first prepared by Michaelis and Polis (*Ber.*, 1887, xx., 54).

During the course of the present research triphenylbismuthine has been prepared in an analogous manner from bismuth bromide in a yield of about 50 per cent. Diphenylbromobismuthine, Ph_2BiBr (m. p. 158°) was simultaneously produced. Michaelis and Marquard (*Ann.*, 1889, ccli., 327) first prepared this substance by the interaction of bismuth bromine and triphenylbismuthine in ethereal solution, and gave the melting-point as 157—158°.

Pfeiffer and Pietsch do not mention the formation of diphenylchlorobismuthine in their experiments.

When treated with magnesium α-naphthyl bromide in ethereal solution, diphenylbromobismuthine dissolves, and a solid is precipitated. Diphenyl-α-naphthylbismuthine has, however, not yet been isolated from the reaction mixture.

Tri-α-naphthylbismuthine, which does not seem to have been previously described, has been prepared from bismuth bromide and magnesium α-naphthyl bromide. It crystallises in almost colourless glistening needles, melting at 235° (uncorr.).

When tri-α-naphthylbismuthine (2 mols.) is treated with bismuth bromide (1 mol.) in ether chloroform solution a golden-yellow crystalline substance separates. This crystallises well from benzene (m. p. 211° uncorr.), and has not yet been analysed, but from its properties and method of formation it would appear to be di-α-naphthylbromobismuthine.

The interaction of bismuth bromide and magnesium benzyl chloride under conditions in which a good yield of triphenylbismuthine is obtained, does not seem to lead to the formation of tribenzylbismuthine, $Bi(CH_2Ph)_3$. A yellow substance containing bismuth, bromine, and organic matter which decomposes without melting and is insoluble in most solvents except glacial acetic acid, is the principal product.

The action of the Grignard reagent on derivatives of quinquivalent bismuth, such as triphenylbismuthine dibromide, Ph_3BaBr_2, is being investigated.

71. "*The Estimation of Mercury as Metal by the Dry Method.*" By ALEXANDER CHARLES CUMMING and JOHN MACLEOD.

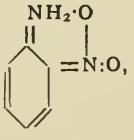
The estimation of mercury as metal by the dry method as ordinarily applied is very troublesome, although it gives accurate results. It is found that the process is simplified, and that equally good results are obtained if the mercury compound is heated in a small Penfield tube with a mixture of lime, iron filings, and lead chromate.

The modified method was applied to the determination of mercury in mercuric chloride, mercuric sulphide, cinnabar, and mercuric iodide; the results were in all cases satisfactory,

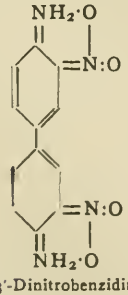
72. "*Studies in the Diphenyl Series.* Part IV. *The Absorption Spectra of the Two Isomeric o-Dinitrobenzidines.*" By JOHN CANNELL CAIN, ALEXANDER KILLEN MACBETH, and ALFRED WALTER STEWART.

A comparison between the absorption spectra of the two isomeric *o*-dinitrobenzidines (Cain, Coulthard, and Micklethwait, *Trans.*, 1912, ci., 2298) and that of *o*-nitroaniline shows that there is a general resemblance between the spectrum of the latter and that of 3 : 3′-dinitrobenzidine, whilst the spectrum of 3 : 5′-dinitrobenzidine differs distinctly from them.

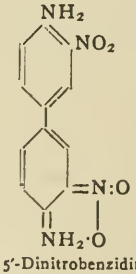
The authors regard *o*-nitroaniline as having the quinonoid constitution :—



and, applying this conception to the case of the *o*-dinitrobenzidines, it was shown that their constitutions are satisfactorily explained by the formulæ :—



3 : 3′-Dinitrobenzidine.



3 : 5′-Dinitrobenzidine.

(These names are retained for convenience of reference).

The constitutions of the isomeric *o*-dinitrodiphenyls and the acetyl derivatives of the isomeric *o*-dinitrobenzidines may be explained in an analogous manner.

73. "*A Novel Method for Resolving Externally Compensated Amines: Derivatives of* d- *and* l-*Oxymethylenecamphor.*" By WILLIAM JACKSON POPE and JOHN READ.

The condensation products which *d*- and *l*-oxymethylenecamphor form with externally compensated hydroxyhydrindamine and α-phenylethylamine can be conveniently employed in the resolution of these bases into their optically active components. It was also shown that α-camphylamine is a pure optically active base with the aid of the same oxymethylene derivatives. *d* Oxymethylenecamphor can be used to effect a ready separation of *d*-bornylamine from the *d-neo*bornylamine which accompanies it.

74. "*A New Iron Bacterium.*" By ERNEST MOORE MUMFORD.

A new bacillus has been isolated from the Bridgewater Canal tunnels at Worsley, Lancashire.

The bacillus designated by the laboratory number, M7, exerts a specific action on solutions containing iron. The organism is a facultative ærobe, and the action on iron solutions varies as the conditions are ærobic or anærobic.

Under ærobic conditions the iron in solution, whether ferrous or ferric, is precipitated as ferric hydroxide. Under anærobic conditions neither ferrous nor ferric solutions are precipitated, but ferric hydroxide already precipitated biologically or chemically is dehydrated and reduced to bog-ore.

In nature these two actions are symbiotic, and are probably the cause of the deposits of bog-ore hitherto attributed to higher bacteria alone.

An enzyme has been separated from the organism by the usual methods, and all the chemical reactions of the living organisms have been reproduced by the enzyme. The optimum of the enzyme is 70°.

Neither the specific action of the organism on iron solutions nor the enzyme are produced in the absence of nitrogen in the medium.

The enzyme is a complex substance containing amino-groups, but the basicity of the enzyme to acids bears no relation to the precipitating power.

The organism is a short round-ended bacillus, 2 microns by 0·4 micron in size. It exhibits a varying motility, and forms endospores and involution forms.

It grows well on ordinary media, the growth on potato of greenish brown nodules being characteristic.

75. "*The Presence of Neon in Hydrogen after the Passage of the Electric Discharge through the latter at Low Pressures.*" By JOHN NORMAN COLLIE and HUBERT SUTTON PATTERSON.

A detailed account of an investigation of which a preliminary note has already appeared (*Proc. Chem. Soc.*, xxix., 22).

76. "*The Double Platinic and Cupric Iodides of Substituted Ammonium Bases.*" By RASIK LAL DATTA.

The author has prepared the *platini-iodides* of rubidium, cæsium, methyl-, ethyl, allyl-, dimethyl-, diethyl-, trimethyl-, triethyl-, tetramethyl-, , and tetraethyl-ammonium, anilinium, and pyridinium. The *cupri-iodides* of tetraethyl- and tetraphenyl-ammonium, pyridinium, and quinolinium were also described.

SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS.

Ordinary Meeting, April 2nd, 1813.

MR. LEONARD ARCHBUTT, President, in the Chair.

MESSRS. Arthur Cecil Bescoby, Thomas Walter Firth Clark, Frank Edward Day, and James Fowler Tocher were elected members of the Society.

A certificate was read for the first time in favour of Mr. Frank Sturdy Sinnatt, 321, Great Clowes Street, Higher Broughton, Manchester.

Certificates were read for the second time in favour of Messrs. Henry Francis Everard Hulton, Charles Thomas Kingzett, and Alfred James Parker.

The following papers were read and discussed:—

"*The Moisture in some English, Colonial, and Foreign Butters during* 1910-1912, *with a Note on the Mitchell-Walker Moisture Test.*" By L. Gowing Scopes.

This paper gives figures for the moisture in 210 samples of butter examined, chiefly Australian, Siberian, and English.

The author has found the Mitchell-Walker moisture test unreliable for estimating water in butter.

"*Egyptian Butter and Semna.*" By S. H. Trimen.

The preparation of semna (clarified butter-fat) is described:—Egyptian semna is usually prepared from buffalo's (gamoose) milk, and is characterised by a high Reichert Meissl figure, average about 33, while Syrian semna is made from goat's and sheep's milk, having a low Reichert Meissl figure and high Polenske number.

The processes for the analysis of butter are discussed, and an unfavourable opinion of the Avé-Lallement method is expressed. Hink's test for cocoa-nut oil is found to give unusual results with buffalo, sheep, and goat butter-fat, goat butter-fat behaving as cocoa-nut oil.

The ageing of semna is accompanied by a slight increase in the Reichert and Polenske values, a large increase in the saponification value, and a large decrease in the Valenta value.

"*Simple Test for Differentiating between Cocoa Butter and 'Green Butter.'*" By Cecil Revis and E. Richards Bolton.

The test proposed by Halphen is not satisfactory in its original form, but by a slight change of the solvent used the method is capable of differentiating between cocoa butter and "green butters" which give similar analytical constants, and may be used for a rough quantitative determination of cocoa butter in admixture with such "green butters."

"*Correct Way to Use Glycerin Jelly in Mounting Micro scopical Objects.*" By L. W. Stansell.

Working in a special manner the difficulty caused by air-bubbles is overcome, and this medium strongly advocated for vegetable structures, the paper showing how to easily prepare with it well-finished mounted slides, and how, also, by a simple expedient to treat the suspended matter in water and the insoluble residue from Demerara sugar.

NOTICES OF BOOKS.

Lecture Notes on Chemistry for Dental Students. By H. Carlton Smith, Ph.G. Second Edition. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1912.

In this book is given a course of lecture notes and practical work for dental students, and in some respects it might be suitable for the use of medical students. Qualitative analysis is first treated fairly fully, the student being supposed to have some acquaintance with the elements of chemistry and with simple experimental work. Dental metallurgy is then taken up and the preparation and analysis of alloys used in dentistry fully described. This section is followed by others on volumetric and microchemical analysis and on local anæsthetics. The chapters on organic chemistry have been very considerably enlarged, and throughout the book many new experiments and illustrations have been added. The attention paid to microchemistry is a good feature, and there are many useful illustrations of the appearance of crystals, &c., under the microscope.

The Russian Year-book for 1913. Compiled and Edited by Howard P. Kennard, M.D., assisted by Netta Peacock. London: Eyre and Spottiswoode, Ltd.

This year book contains very copious statistics showing the activity and resources of the Russian Empire, and long and detailed accounts are given of the state and progress of agriculture and other industries, of means of communication, ports, shipping, &c. Trade reports are included and finance is fully discussed. It is difficult to see how the year-book could be made more complete in any respect, and the third issue is worthy of as good a reception as its predecessors.

The Letters Patent Insurance Company, Ltd. King's House, Kingsway, London, W.C.

This booklet explains how manufacturers and patentees, by availing themselves of the services of the Letters Patent Insurance Company, Ltd., may make themselves perfectly secure against all risk of infringement. The Company possesses a staff of expert advisers, and is prepared to supply reports on patents submitted to them for consideration, and also to insure them. Thorough search will be made into both British and foreign patent literature, and reports will be made as to the utility and novelty of any invention; the examiners will even make suggestions in cases in which patents have not yet been granted, and the Company undertakes negotiations for settlement of impending actions and for the amalgamation of kindred interests. The schedule of annual premiums of policies from £100 to £12,000 is given in the booklet.

Abstract Bulletin of the Physical Laboratory of the National Electric Lamp Association, Cleveland, Ohio. Published by the Laboratory. January, 1913.

The laboratory of the National Electric Lamp Association was organised in 1908 to stimulate the development of those branches of science with which the art of lighting is closely connected. Much valuable research work in physics and physiology has been done in the laboratory, and reports of it have been published from time to time in various scientific and technical journals, such as the *Electrical World*, the *Physical Review*, the *Astrophysical Journal*, and the *Philosophical Magazine*. The Director, Mr. E. P. Hyde, has now considered it advisable to prepare a complete record of the work of the laboratory, and accordingly this volume of *Abstract Bulletins* has been issued, containing abstracts of the results of all the investigations undertaken in the laboratory, written by the authors of the original papers. When sufficient material has accumulated it is hoped that a further volume may be published.

CORRESPONDENCE.

THE ANTISEPTIC USE OF GUAICOLATE OF PIPERIDIN IN MILK.

To the Editor of the Chemical News.

Sir,—Anent a recent communication in the Chemical News on the antiseptic and preservative use of bichromate of potash and phenol in milk, I would call attention to the highly probably successful application of guaicolate of piperidin in milk as an internal antiseptic for use in this way for phthisical subjects, and its application as possibly suitable in a general way as harmless and a preservative.—I am, &c.,

J. C. Thomlinson, B.Sc.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Seances de l'Academie des Sciences. Vol. clvi., No. 5, February 3, 1913.

Reactions Accompanying Osmosis of Hydrogen through Iron.—G. Charpy and S. Bonnerot.—When a current of hydrogen is passed for some time over iron no appreciable quantities of the gas are absorbed, and probably irons and steels which are kept in air are generally saturated with hydrogen. If, however, the passage of the gas is prolonged for a very long time the metal gradually softens, owing to the fact that the hydrogen exercises a reducing action on certain substances contained in the metal. Thus iron can be purified by passing hydrogen over it.

Action of Alkaline Sulphites on Ethylenic Acids.—J. Bougault and Mouchel-la-Fosse.—Many ethylenic acids combine with sodium bisulphite to give the sodium salts of sulphonic acids, by the fixation of $HNaSO_3$ at the double bond:—

$$R.CH=CH.R' + SO_3NaH = R.CH_2.CH(SO_3Na).R'.$$

The fixation of $NaHSO_3$ is more rapid the more electronegative groups the ethylenic acid contains. The sulphonic acids obtained are very soluble in water, even when they are derived from insoluble acids. The amount of ethylenic acid in a mixture with saturated acids can be determined by heating the mixture with a solution of sodium sulphite and titrating the quantity of sulphite combined.

Berichte der Deutschen Chemischen Gesellschaft. Vol. xlvi., No. 1, 1913.

Mercury Dibenzyl.—Paul Wolff.—Mercury dibenzyl can be prepared by Grignard's method. It crystallises in long glittering white needles, which melt at 111° and dissolve readily in alcohol, ether, chloroform, benzene, &c. When heated above its melting-point it decomposes into mercury and dibenzyl. When heated with dihalogen mercury in alcoholic solution a benzyl residue is replaced by halogen: $(C_6H_5.CH_2)_2Hg + HgCl_2 = 2C_6H_5.CH_2.HgCl$.

Nitrate and Nitrite Assimilation.—Oskar Baudisch and Erwin Mayer.—If a solution of potassium nitrite and formaldehyde is exposed to diffused daylight alkaloidal compounds are formed. They probably contain a pyridine ring and a pyrrol or pyrrolidine ring. While H_2CO_3 is reduced to H.COH chiefly through the agency of the yellow and red rays, it is the blue, violet, and ultraviolet rays which reduce nitrates to $N\lessgtr^{O}_{H}$.

Adsorption of Acetylene by Palladium Black.—C. Paal and Christian Hohengger.—The authors have investigated the behaviour of acetylene towards palladium black in pure aqueous solution, and also towards dry palladium black. In both cases adsorption occurs, but apparently the acetylene is not adsorbed unchanged but is gradually converted into polymerisation products of unknown composition.

Separation of Arsenic and Tungsten.—Siegfried Hilpert and Theodor Dieckmann.—Solutions of potassium arsenate and sodium tungstate were mixed and heated on the water-bath for an hour. Then cuprous chloride and hydrochloric acid were added, and the whole was evaporated down to a small residue. Distillation with hydrochloric acid was then performed twice, and the arsenic determined in the distillate by means of iodine. It was found that the method gave the most accurate results if, after the second distillation, the residue was treated with strong alkali and then re-distilled with hydrochloric acid.

Atti della Reale Accademia dei Lincei. Vol. xxi. [ii.], No. 11, 1912.

Compounds of Halogen Salts and Phosphates of Metals.—Mario Amadori.—Phosphate and fluoride of lead form a compound, $PbF_2.3Pb_3(PO_4)_2$, the melting-point of which (1046°) is higher than that of either constituent. In all probability this compound can exist in three modifications. The author has observed one temperature of transformation, viz., 696°. The phosphate exists in two modifications, the temperature of transformation being 782°. The chloride and phosphate of lead form a compound of similar composition. Its fusion point is above 1100°. The compound of fluoride and phosphate corresponds to the calcium salt found in nature (apatite), and that of the chloride and phosphate to pyromorphite. No compound of the type of wagnerite has been detected by thermic analysis.

New Oxime of Santonine.—Guido Cusmano.—Canizzaro has already prepared one of the stereo-isomeric oximes of santonine. The other can be obtained by heating the α-isonitrammine oxime of santonine with sodium hydrate. The new oxime melts at 230°, undergoing decomposition. It is soluble in water, very soluble in alcohol; it crystallises with one-and-a-half molecules of water. It dissolves in caustic alkalis, and the solution when treated with the molecular quantity of strong hydrochloric acid deposits a santoninic acid.

MISCELLANEOUS.

The Chadwick Public Lectures, 1913.—Two evening lectures, with epidiascope illustrations, on "The Evolution of Epidemics" (Nineteenth Century—Specificity and Evolution; Present Day—Scientific Evidences of Evolution), will be given by Dr. J. T. C. Nash, D.P.H.(Camb.), County and Chief School Medical Officer of Health for Norfolk, at the Royal Society of Medicine, 1, Wimpole Street, W., on Mondays, April 14th and 21st, at 8.15. Sir Richd. Douglas Powell, Bart., K.C.V.O., M.D., F.R.C.P., will preside on the 14th, and Sir William J. Collins, M.D., M.S., B.Sc., F.R.C.S. (Chairman of the Chadwick Trust), on the 21st. Admission free.

MEETINGS FOR THE WEEK.

MONDAY, 14th.—Royal Society of Arts, 8. (Howard Lecture). "Aeronautics," by Prof. J. E. Petavel, F.R.S.

TUESDAY, 15th.—Royal Institution, 3. "The Heredity of Sex and some Cognate Problems," by Prof. William Bateson, F.R.S., &c.

WEDNESDAY, 16th.—Royal Society of Arts, 8. "The Physical Properties of Clay," by Walter C. Hancock, B.A.

THURSDAY, 17th.—Royal Institution, 3. "The Progress of Hittite Studies—Recent Explorations," by Prof. John Garstang, M.A., &c.

—— Royal Society of Arts, 4.30. "The Burma Oil Fields," by N. G. Cholmeley, C.S.I.

—— Royal Society. "Luminosity Curves of Persons having Normal and Abnormal Colour Vision," by W. Watson. "Fluorescence Spectrum of Iodine Vapour," by J. C. McLennan. "Relation between the Crystal-symmetry of the Simpler Organic Compounds and their Molecular Constitution," by W. Wahl. "Purification of Phosphorus Pentoxide for Use in High Vacua," by J. J. Manley.

—— Chemical, 8.30. "Action of Tartaric Acid on Tin in the Presence of Oxygen," by A. Chaston Chapman. "Reaction between Ferric Salts and Thiocyanates," by J. C. Philip and A. Bramley. "Preparation of Pure Bromine," by A. Scott. "Preparation of Conductivity Water," by R. Bourdillon. "Constitution of the Anhydro-bases derived from Tetrahydroberberine Alkyl Hydroxides," by F. L. Pyman. "Application of Hofmann's Reaction to Dialkylacetamides," by F. L. Pyman. "Derivatives of *o*-Xylene," by J. L. Simonsen. "Synthetical Production of Derivatives of Dinaphthanthracene," by W. H. Mills and M. Mills.

FRIDAY, 18th.—Royal Institution, 9. "Applications of Polarised Light," by T. M. Lowry, D.Sc.

SATURDAY, 19th.—Royal Institution, 3. "Boccacio," by Prof. Sir Walter Rayleigh, M.A.

THE CHEMICAL NEWS.

Vol. CVII., No. 2786.

THE CHEMISTRY OF THE FLORAL PIGMENTS.

By P. Q. KEEGAN, LL.D.

Gardeners and many persons have wondered why scientific inquiries have not been made into the subject of the colours of flowers. The attempt to institute such an inquiry may perhaps be usefully preceded by a brief sketch of certain published work of this kind, which may be deemed scientific. Thus, in 1860, the French chemist Filhol, after an examination of the pigments of red, rose, and blue flowers, concludes that they are due to one substance (cyanine), notwithstanding certain differences in their reactions towards alkalis. Berzelius had decided that the red pigments of cherries, gooseberries, &c., were actually and originally red, *i.e.*, they were not a combination of a blue pigment with an acid, as had been previously maintained. It had been known for many years before that blue flowers were reddened by acids, and that the natural tint of rose or faintly red flowers was made more vivid and brilliant by the addition of a trace of acid; but, of course, on the assumption that the whole of the floral pigments were merely modifications of only one fundamental substance (chlorophyll, for instance), these facts seemed comparatively insignificant. In 1850 Morot expressly denied that the green matters of leaves were directly connected in any way with the red and blue matters, and in this opinion he was strongly followed up and supported by Morren in 1858, and he also insisted that the red colour was not derived from the blue, although he allowed that the former may probably be an alkali salt of the latter. It now became clear that no further advance could be made until the mystery of the actual cause (chromogen) of these colorations could be revealed. This admirable feat was accomplished, in the first instance apparently, by Wigand in 1862; he expressly states, as the result of his researches, that—"A colourless substance dissolved in the cell sap provides the basis for anthocyan, and this chromogen is tannin, or rather some modification of tannin; the transformation of cyanogen into anthocyan depends on an oxidation." It was not very creditable that this most fruitful suggestion remained practically ignored in Germany for nearly twenty years. The efforts, however, of such acute observers as Kraus, H. Pick, and Wiesner gradually revived it, and the further marvellous progress made in the chemistry of the organic pigments finally established the fact beyond question that the almost universally present tannoids or tannins of plants possess a chromogenic nucleus of a phenolic nature capable, according to its composition, of evolving all the various red and blue colorations of flowers, fruits, and leaves.

It was necessary, however, to effect a certain kind of synthesis in order to verify the fact that the pigments originated in tannin as a chromogen, and this feat was executed apparently, or at least published, in the first instance, by A. Gautier in 1877. Working in conjunction with M. Girard on the cautious oxidation of the tannins, he concluded that the red colouring matter of wine is only one of the transient products of oxidation of œnotannin (tannin of the grape pulp or pellicle). Later on, in 1906, he stated that the pigment of the vine or of the leaves of Virginia creeper is formed by acid phenols of the nature of tannins. Some time previously to seeing these publications, I had observed that on carefully heating the colourless aqueous solutions of the tannins of sycamore, horse chestnut, wild cherry, dock, &c., with dilute hydrochloric acid, a fine red soluble pigment was formed, which, on treating with slight excess of dilute ammonia or baryta water, assumed a green tint, exactly in the same way as the red pigment extracted from red autumn leaves behaved. It was assumed, therefore, that the red colouring matter of leaves and flowers originated in a similar way, *i.e.*, that the tannin contained therein underwent a similar change brought about by natural agencies. It may be considered, in fact, as established that all tannins possess a chromogenic nucleus of a phenolic nature which, by the action of the air or other oxidising media *in vitro*, is capable of producing a coloration more or less pure. But it may also be assumed that the protoplasm of the plant itself is likewise capable, by an organic process of deassimilation, of producing, in a sufficiently oxidising medium, colorations of a more vivid and brilliant description and on a higher and purer scale than those induced by mere external or inorganic agencies. In this case, however, it would appear that the actual mechanism, *i.e.*, the possible play of the surroundings on the phenomena, is only indirect; *i.e.*, if an external oxidising medium is necessary for the production of the phenomena, it is supplied by the organic action of the plant itself, but not perhaps exclusively in all cases.

It is known that in the annual plant, like as in the young forest leaf, there is produced at first a distinctly chromogenic substance properly called a tannoid, such as quercitrin, rutin, luteolin, gentisin, galangin, &c., which carry a ketone CO group forming with O a closed ring, acting thus as a strong chromophore, which is reinforced by several HO groups (auxochromes) in the molecules, the whole possessed of considerable tinctorial power as respects orange, yellow, and brown tints and shades. None of these tannoids, however, are chromogens of the blue, red, pink, or purple colorations of flower and leaf. For this latter purpose it is evident that some other structure of the molecule or arrangement of atomic groups must be provided. This can be conceived as being effected in two different modes, viz., (1) by a condensation or polymerisation of a tannoid previously existing in the cells of flower or leaf, or (2) by a specially more efficient process of deassimilation occurring in the protoplasm thereof itself. Now, there may be some difficulty in deciding as to which of these two modes of action is operative in the case, but it is extremely doubtful if the first mentioned has got anything to do with it. True it may be that that in the same fully developed corolla there may co-exist side by side a tannoid and a tannin coloured (anthocyan) or colourless, but this is no proof that the latter has been derived from the former; they may have been formed at different periods of the flower's existence, and numerous analyses induce me to conclude that this has actually been the case. In fact, a colourless tannoid or tannin may be always extracted without the aid of decolorisers from all corollas however deeply tinted they may naturally be. In the floral bud a little tannoid is found on the external side of the young petals, *i.e.*, on the side furthest away from the gymnœcium, but eventually the red or blue pigments appear in both epidermises as well as on the bundles—facts which indicate a wider distribution and production of the tannic chromogen. The physiological law that governs the formation of the soluble pigments of flowers is, that processes of special deassimilation are carried on in certain cells when certain adjacent cells are in urgent need of nitrogenous nutriment; for instance, those of the stamen and pistil at the period of their ever progressive development, at the period of fecundation, and as preparatory to the formation of ovules and seeds, &c. Hence here a powerful drain on the albumenoids of the corolla is induced, whose molecules therefore break up, the nitrogenous nuclei thereof separate and pass over as much as is needed to the cells of the vigorously active pistils and stamens, while the aromatic nuclei remain behind as tannic chromogen, the precursor of the brilliant blues, reds, violets, and purples. It is hardly necessary to state that the corolla is the seat of a very active oxidation, while the reductive processes of assimilation therein are almost nil.

With respect to the chance or probability of a red, pink,

vivid violet, or purple coloration being evolved, in contrast to a pure blue one, in any particular corolla, the following propositions may be formulated, viz. :—(1) A blue flower is unproducible in species which are capable of forming or contain phlobaphenic tannin, howsoever the inflorescence may be developed as respects dimensions, weight, or delicacy of structure. (2) A blue flower is more likely to be produced in a species provided with a gamopetalous corolla or perianth, and therefore more competent to evolve and develop to the full a certain quantum of a polyhydric chromogen. (3) In species wherein the tannin natural to the organism is iron-greening and phlobaphenic, a pseudo-blue flower may be evolved, even in a polypetalous slow-growing corolla, under the form of a vivid violet or of a purple tint or shade only faintly reddish. Many species of genera, such as phlox, habitually exhibit red flowers which really might be true blue, but the corolla is rarely spacious in such cases.

The extremely interesting and hitherto unsolved question respecting the chemical origin of the true blue pigment of flowers must now be considered. A genuine blue is undoubtedly the *chef d'œuvre* or the *coup de grâce* of Nature's art, and therefore we must expect to find something rare and extraordinary in the special means adopted in the plant for its accomplishment. Reverting to the causes aforesaid of the production of red tints in corollas, we find that the tannic chromogens therein concerned with their ketonic and hydroxyl groups are quite sufficient for the purpose ; but is this structural provision of the molecule alone competent to evolve the magnificent true blues of the gentian, campanula, centaurea, pulmonaria, salvia, &c. ? Are the hydroxyl groups too feeble as chromophores, or perhaps a biketone is needed in place of a mere single CO group ? Various analyses and analogical considerations lead to the conviction that the molecule of the blue chromogen must needs possess a certain building up of carbon atoms ; for instance, a side chain of three carbon atoms might suffice ; a quinonic structure or an accession of hydroxyls would most probably only deepen the red, or even produce a glaring orange in certain circumstances. Some of the oak phlobaphenes contain seven HO groups, but are dull brown in colour, and none of the anthraquinones or their derivatives found in plants give bright blue dyes or colorations. It would therefore seem to be evident that an excessive number of carbon atoms in the molecule of the chromogen would be fatal to the production of the effect. But let us now examine the plants themselves.

In the first place, we must call in the aid of classification, *i.e.*, we must search and see in what particular genus, order, and alliance those particular species are enrolled which habitually exhibit true blue flowers ; and then, having decided this question, we subject these plants to analysis in order to detect whether they habitually produce a certain special kind of tannin in large or small quantities. If we do actually demonstrate that a special kind of tannin is evolved by these plants which is not evolved by non-blue flowering plants, then we may conclude fairly confidently that we have really discovered the presiding chromogen of the blue pigment. My own extensive researches in this direction, coupled with those of others, seem to point unequivocally to that particular tannin termed caffetannin as the actual chromogen of the true blue pigment of flowers. Concerning this tannin it may be stated that it is not a glucoside, and that it has been denied that it is a fixed or homogeneous principle. However, it has a CO group and six hydroxyl groups, two of which are in the para-position (quinol), and two others in the ortho-position (catechol), relative to each other ; there is also a lateral group of three carbon atoms, viz., $CH=CH\cdot COOH$, which seems to show a definite relationship with styrene, $C_6H_5(CH=CH_2)$. It would appear, however, that the conjunction of the catechol and quinol hydroxyl groups with the CO and COOH groups would alone or merely evolve a brownish or deep red coloration. Therefore, it would seem that it is the approach and relationship of caffetannin to styrene that imparts to it the most interesting specific property of functioning as a chromogen of the true blue pigments of flowers. Many of the plants which contain this tannin also contain cinnamic acid, free or combined as an ester, &c., and this acid is related to styrene as benzoic acid is to benzene, the side-chain, characteristic of styrene, carrying with it apparently the capacity to evolve a blue pigment. With regard to the systematic position of those particular plants which are competent to evolve a true blue corolla, it may be stated that the alliances known as Personales, Lamiales, Polemoniales, Gentianales, Campanales, Asterales, Rubiales, Umbellales, and certain Ranales are all supreme in this respect among Dicotyledons. With regard to Monocotyledons the Liliaceæ are the only order which the present condition of research would warrant any general conclusion being formed, inasmuch as in the resins of this order cinnamic acid both free and combined has been detected, and hence it is extremely probable that caffetannin occurs likewise in the cells of some of the species at all events, as, for example, in the lily of the valley found there by Charaux, and confirmed by myself. In many plants this tannin occurs in very small quantity, sometimes as low as 0·12 per cent in the dry leaf ; but this is not surprising when the enormous oxidation necessary to its formation is taken into account. Although caffetannin is the only known tannin (gallotannin alone excepted) which yields oxidative blue compounds with bases, it is questionable if in the natural coloration of the corolla the presence of an inorganic base is requisite for the result, as it has been found that *Phlox decussata* watered with 1 per cent alum solution does not give blue flowers, though it does so apparently with Hydrangea, the chromogens in these cases being quite different. Many species of Phlox are of a vivid red which could or ought to be blue, and it is rather difficult to explain this fact otherwise than by the circumstance, proveable by other facts, that these plants have a natural tendency to produce acids as products of deassimilation. On the other hand, it may just be this tendency which in other cases, *e.g.*, the Leguminosæ, common flax, &c., induces the formation of vivid violets and purples in lieu of pinks or reds ; the effect in the former instance being perhaps due to traces of free acid, and in the latter to the attraction by the corolla of an excess of base, thereby yielding a faintly alkaline reaction in the cells. Indeed, as shown by experiment upon the purified aqueous extract of a bright red rose, for instance, a mere neutralisation of the acid present therein by bicarbonate of soda (non-alkaline to phenolphthalein) is sufficient to change the red tint to a beautiful pseudo-blue, *i.e.*, it requires a trifle more base only.

THE PRESENT STATUS OF THE TEMPERATURE SCALE.*

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(Concluded from p. 171).

Examples of Standard Temperatures.—Some of the standard temperatures, owing to their great importance, have been determined many times, and are therefore particularly valuable as primary reference points. The actual status of our knowledge of the temperature scale is perhaps best illustrated by giving in detail the measurements since 1900 on some of the most carefully studied of these temperatures, such as the boiling-points of oxygen and sulphur and the melting-points of cadmium, gold, platinum, and tungsten (see Table IV.).

International Temperatures.—It is evidently of the greatest importance for chemists and others who have to express or locate many of their results in terms of tem-

* Original communication, *Eighth International Congress of Applied Chemistry*, xxii., p. 53.

Table IV.

Date.	Observer.	Method.	Temperature. Observed.	Thermodynamic.
		Oxygen Boiling-point = −182·9.		
1901	Holborn	H (*a*) scale constant vol.	+182·7	
1901	Dewar	H (*a*) scale constant vol.	−182·5	
1906	Grummach	Pentane thermometer	−182·66	
1906	Travers, Jaquerod, and Senter	H (*a*) scale constant vol.	−182·93	−182·87
		He scale constant vol.	−182·8	
1908	Kammerlingh Onnes and Braak	H (*a*) scale constant vol.	−183·04	−182·99
		Sulphur Boiling-point = 444·6.		
1902	Chappuis and Harker	N (*a*) scale constant vol.	444·7 (*b*)	444·8
1908	Eumorfopoulos	Air scale constant pressure	444·55 (*a*)	444·93
1911	Holborn and Henning	H (*a*), He, constant vol.	444·51 (*b*)	444·51
		N constant vol.	444·39	
1912	Day and Sosman	N (*a*) scale constant vol.	444·45 (*a*)	444·55
1912	Dickinson and Mueller	(Day and Sosman's thermometer)	444·28 (*b*)	444·38
		Cadmium Melting-point = 320·92.		
1900	Holborn and Day	N (*a*) scale constant vol. (*b*)	321·7	321·8
1902	Kurnakow and Puschin	Thermocouple interpolation	321·8	
1904	Day and Allen	Thermocouple interpolation	321·7	
1909	Waidner and Burgess	Pt resistance (S.B.P. = 444·60) (*a*)	320·94	320·94
1910	Day and Sosman	Thermocouple extrapolation (*b*)	320·0	320·1
1911	Holborn and Henning	H (*a*), He, N (*a*) scales constant vol. (*a*)	320·92	320·92
1912	Day and Sosman	Corrected from 1910 value (*b*)	320·8	320·9
1912	Adams and Johnston	Cu-Cn thermocouple interpolation	320·92	320·92
		Gold Melting-point (*c*) = 1063 (*d*).		
1900	Holborn and Day	N (*a*) scale constant vol.	1064·0	1064·3
1902	D. Berthelot	Air-optical constant pressure	1064	1065·6
1904	Jaquerod and Perrot	Air, CO, N (*a*), O (*a*) constant vol.	1067·2	1067·4
1908	Day and Clement	N (*a*) scale constant vol.	1059·3 (*e*)	1059·5
1910	Day and Sosman	N (*a*) scale constant vol.	1062·4	1062·6
		Platinum Melting-point = 1755 (*Basis:* C_2 − 14,500).		
1903	Nernst	Total light from black body	1782	
1905	Holborn and Henning	Combined optical and thermoelectric	1729	
1905	Harker	Thermoelectric	1710	
1906	Nernst and Wartenberg	Optical (Wien's law)	1753	
1907	Holborn and Valentiner	Optical (Wien's law)	1760	
1907	Waidner and Burgess	Optical (Wien's law)	1753	
		Radiation from Pt, three colours	1750	
		Thermoelectric (various formulæ)	1697—1757	
1909	Féry	Radiation from Pt: Oxidising at	1690	
		Reducing at	1740	
1910	Sosman	Thermoelectric extrap. from Pd = 1549	1752	
1910	Ruff	Optical about	1750	
		Tungsten Melting-point = 3000 (*Basis:* C_2 = 14,500).		
1906	Waidner and Burgess	Wien's law, lamp filament	3200	
1907—10	Waidner and Burgess	Wien's law, lamp filament	3080—3050	
1907	Wartenberg	Wien's law, Wenhelt discharge	2930	
1910	Pirani	Wien's law, lamp filament	3226	
1910	Ruff and Goecke	Wien's law, in vacuum furnace	2597	
1911	Forsythe	Wien's law: With wedge	2974	
		With vacuum furnace	3030	
1911	Pirani and Meyer	Wien's law with filament and strip	2997	
1911	Langmuir	Total photometric	3177	

(*a*) Transferred by platinum resistance thermometer.
(*b*) Transferred by Pt-Rh thermocouples.
(*c*) All measurements were made by transfer with Pt-Rh thermocouples.
(*d*) Several determinations of the copper melting-point (1083) have also been made, and auxiliary methods have shown Cu—Au = 20°, so that the gold point is better known than the table would indicate.
(*e*) Sample shown to contain iron from crucible.

peratures, that they be able to do so in terms of a common scale, as otherwise confusion reigns when endeavouring to compare the numerical values assigned by different observers to the various phenomena.

For the past twenty-five years, thanks to the International Bureau of Weights and Measures, it has been possible to express results to 0·002° C. within the fundamental interval 0° to 100° C., but outside this interval chaos has reigned.

Both at low temperatures and high, there have been almost as many scales as observers, and some of the outstanding differences were relatively very large, even within the past year, for example, 1° at the sulphur boiling-point and 7° at the gold melting-point.

The recent series of investigations mentioned above have rendered it possible, however, to greatly reduce the uncertainties, and the state of the art of temperature measurements is now such that it should not be difficult for the various standardising laboratories to agree upon a common temperature scale which would be defined in some such manner as outlined above. In pursuance of this idea, the several national laboratories and the International Bureau are at present interchanging communications relative to the establishment by agreement of some such single temperature scale, and it is to be hoped that the outcome of these interchanges will be of great practical benefit and convenience for the certification and use of temperature-measuring instruments, and that thenceforth 500° C. or 1000° C., for example, will each convey but one idea of temperature as do 0° or 100° C. at the present time.

AN ELECTROLYTIC THEORY OF THE CORROSION OF IRON.*

By BERTRAM LAMBERT, M.A.

THE application of electrolytic ideas to the question of the corrosion of iron has been discussed by Whitney (*Journ. Am. Chem. Soc.*, 1903, xxv., 394), Cushman (*Trans. Am. Elektrochem. Soc.*, 1907, xii., 403), Tilden (*Trans. Chem. Soc.*, 1908, xciii., 1356), Walker (*Journ. Iron and Steel Inst.*, 1909, i., 70), Armstrong (*Science Progress*, 1911, xxii., 311), and many others, but much confusion and misunderstanding has arisen owing to the different interpretations used by the various writers.

The American writers have discussed the question from the standpoint of Nernst's conception of the source of electromotive force between a metal and a solution. It seems to follow from their reasoning that all iron (even if it be chemically pure and physically homogeneous) ought (*a*) to rust in contact with air (or oxygen), (*b*) to cause the deposition of copper from solutions of copper salts.

The present writer's experiments (*Trans. Chem. Soc.*, 1912, ci., 2068, *et seq.*) have proved beyond any doubt that iron can be prepared which will not rust on long exposure to air and water (either distilled or ordinary tap-water), and will not cause the deposition of copper when placed in even strong solutions of copper sulphate or copper nitrate under ordinary conditions.

It also seems to be thought by many supporters and opponents of electrolytic theories that any electrolytic theory of the corrosion of iron must "stand or fall" on the question of the solubility of iron in pure air-free water.

The object of this paper is to show that a simple and natural development of the ideas of Faraday on electrolysis will give us the beginnings of a satisfactory theory of the corrosion of iron—a theory incomplete as yet owing to the lack of experimental facts, but one which is quite in accordance with well established facts, and which is not affected by the question whether iron is soluble to any appreciable extent in pure air-free water.

It is well known that whilst ordinary commercial impure zinc readily dissolves when placed in dilute sulphuric acid, the pure metal is scarcely affected unless metallic connection is made between it and another more electro-negative metal, either within or without the liquid. Under these conditions the pure zinc dissolves, but the action ceases immediately the metallic contact between the pure zinc and the more electro-negative element is broken.

In impure zinc the more electro-negative element is already present within the mass of the metal, in the form of minute impurities, such as copper or lead, or perhaps as another form of the metal which is relatively electro-negative to the main mass of the metal.

Whenever we have two metals (or two modifications of the same metal) which are electrically different, that is, have different solution pressures, and they are placed in metallic contact in an electrolyte, then the relatively electro-positive part will dissolve with the production of an electric current flowing through the electrolyte from the electro-positive to the electro-negative pole, and in the opposite direction through the metal.

The rate of such a reaction depends (*a*) on the magnitude of the difference of electric potential—that is, the difference of solution pressure between the two metals or the two modifications of the same metal, and (*b*) on the resistance offered by the electrolyte to the passage of the electric current.

No part of the metal can dissolve unless an electric current actually passes through the electrolyte. The rate of the reaction may, however, be so infinitesimal that the amount of metal passing into solution will not be sufficient to respond to chemical tests even after long periods.

Let us consider, in this light, the case of a piece of ordinary commercial iron in contact with the electrolyte water.

Such a piece of iron is impure and not homogeneous—there are some parts of it which have a different solution pressure from other parts, and so when it is placed in contact with the electrolyte water we have all the conditions for the production of an electric current.

If the conditions are such that an appreciable electric current can pass between the two electrically different parts of the iron the metal will dissolve at the relatively electro-positive parts. The fact that iron is practically insoluble in pure water (in the absence of oxygen) shows that the current which actually does pass is so infinitesimal that the amount of iron dissolved cannot be detected, even after long periods, by chemical means.

This may be due to two causes, namely, (*a*) the small magnitude of the electromotive force owing to the small differences of potential between the electrically different parts of the metal, and (*b*) the great resistance offered to the passage of an electric current by the electrolyte.

The writer's experiments (*loc. cit.*, pp. 2056 *et seq.*) seem to be generally accepted as proving beyond any doubt that commercial forms of iron will undergo corrosion quite readily in contact with pure water and pure oxygen in the complete absence of carbonic acid or any other acid—that the only essentials for the corrosion of ordinary iron are water and oxygen. It is generally believed that iron must pass through a process of solution before rust is produced, and so, whilst the metal is practically insoluble in pure water alone, it must be soluble in the presence of oxygen. It follows, then, that oxygen must bring about some alteration in the conditions of the "voltaic circle"—commercial iron and water—in such a way that a greatly increased electric current passes between the electrically different parts of the iron. That oxygen can bring about such a change of conditions is beautifully illustrated by an experiment described by Dunstan and Hill (*Trans. Chem. Soc.*, 1911, xcix., 1853). Cushman ("Amer. Soc. Testing Materials," 1907) has shown that if a piece of commercial iron is left in contact with a solution of sodium chloride to which a little phenolphthalein has been added, a pink colour develops in the solution which is in contact with some parts of the metal. These colour zones, which are

* A Paper read before the Faraday Society at the Manchester Meeting, April 4, 1913.

always confined to a portion (or portions) only of the metal, indicate the presence of hydroxyl ions (or free alkali) at these points. After being kept some time, the metal beneath the pink zones remains quite bright, but corrosion takes place gradually at the other parts of the metallic surface. This experiment shows that the solution is being electrolysed, and that the iron is passing into solution at those parts not marked out by the pink colour of the phenolphthalein. It shows also that some parts of the iron are electrically different from other parts, and that the electromotive force produced by these differences of solution pressure is enough, under these conditions, to cause the passage of an electric current of sufficient magnitude to produce perceptible electrolysis of the solution of sodium chloride.

It was shown by Dunstan and Hill, however, that the extent of this electrolysis was conditioned by the presence of oxygen, because, in the absence of air (or oxygen) the pink zones were not developed, and therefore an electric current sufficient to produce perceptible electrolysis could not pass.

Oxygen therefore must do one of two things—it must in some way or other increase the electrical differences between the parts of the metal and so increase the electromotive force, or it must reduce the resistance of the circuit. When a piece of commercial iron is put into water in a vacuum, iron strives to pass into solution at the relatively electro-positive part of the metallic surface, but hydrogen, produced by the electrolysis of the water, is deposited at the relatively electro-negative part. This film of hydrogen, forming almost instantaneously and covering up the negative pole, introduces an enormous resistance into the circuit, and reduces the electric current to an almost negligible strength, so that the rate at which the iron passes into solution is infinitely small.

Oxygen dissolved in the water probably acts by oxidising the hydrogen thus deposited at the negative pole—destroying the polarisation—and so allowing a greater current to pass between the electrically different parts of the metal.

If this argument is true, then commercial iron ought to pass into solution, *in the absence of oxygen*, if it is placed in an electrolyte, such as copper-sulphate solution, where, instead of the non-conducting hydrogen film, there would be a conducting film of metallic copper produced at the relatively electro-negative pole. Experiment shows this to be true. Commercial iron, when brought into contact with a solution of pure copper sulphate in a vacuum, causes the immediate deposition of copper on the iron just as readily as when the experiment is conducted in the presence of air; in a short time all the copper is removed from the solution, and iron takes its place.

It seems to be clear, then, that when commercial iron rusts in contact with air and water, oxygen plays an important part in the actual dissolving of the iron, quite separate and distinct from its later function of converting the dissolved iron into rust.

The formation of rust from the dissolved iron is not, as is sometimes supposed, a simple oxidation of the ferrous ions. It is not possible for the ferrous ion to be oxidised to the ferric ion by means of ordinary molecular oxygen. This can readily be proved by a simple experiment. If a solution of ferrous sulphate is made strongly acid with sulphuric acid, and oxygen is passed through the solution, comparatively little ferric salt will be found in the solution even after the oxygen has been passed through it for several days. The greater the proportion of free sulphuric acid present, the less the oxidation which takes place. The oxygen only oxidises the undissociated ferrous hydroxide formed by the hydrolysis of the ferrous salt, and since ferrous hydroxide is a very weak base, hydrolysis is very considerable unless a large excess of acid is present.

In the rusting of iron, then, the metal passes into solution as ferrous ions owing to electrolytic action between the electrically different parts of the iron, oxygen playing an essential part in the process. The ferrous ions then combine with the hydroxyl ions present in the water to form undissociated ferrous hydroxide, $Fe + 2OH = Fe(OH)_2$.

At this stage oxygen plays a second part, converting the ferrous hydroxide into ferric hydroxide or some hydrated form of ferric oxide (rust),—

$$4Fe(OH)_2 + O_2 + 2H_2O = 4Fe(OH)_3.$$

The fact that iron rust produced under ordinary atmospheric conditions is shown, on analysis, to contain carbonic acid—that rust formed under such conditions is a basic carbonate of iron—does not necessarily prove, as has been supposed, that carbonic acid plays any essential part in its formation. Wet ferric hydroxide absorbs carbon dioxide, so that the carbonic acid found in rust formed under these circumstances may very probably have been absorbed from the air by the rust after its formation.

It follows from the theory that if we could produce metallic iron chemically and physically homogeneous it ought not to rust, because there would not be any difference of solution pressure on its surface, and therefore no cause for the production of electric currents when the iron was placed in an electrolyte.

It would follow also from the theory that the production of a coherent and absolutely homogeneous coating, of whatever nature, on the surface of commercial iron would prevent corrosion. The bearing of this on the question of passivity is discussed later.

The Properties of Chemically Pure Iron considered in connection with the Electrolytic Theory of Corrosion.

The present writer (*Trans. Chem. Soc.*, 1910, xcvii., 2430; 1912, ci., 2068) has prepared chemically pure iron, and it has been found that such iron can be exposed to the action of air (or oxygen) and water (either distilled or tap-water) for an apparently indefinite time without showing any signs of corrosion. It must be strongly emphasised, however, that *chemical* purity is not the only essential.

In the preparation of pure iron by the writer's method the same sample of ferric nitrate, treated in exactly the same manner throughout its conversion into iron, will not always give like specimens of the metal.

One batch of iron will rust quite readily, whilst another batch can be exposed for many months to the action of air and water without showing any signs of corrosion. All the pieces of the same batch behave, as a rule, in a precisely similar manner. Now, any difference between the batches cannot be due to differences in *chemical* composition. The only possibly variable factors are temperature of reduction and rate of cooling, and so differences in the product must be of a *physical* and not of a chemical character.

It is a very striking fact that the pieces of iron which will not rust can also be put in solutions of copper sulphate or copper nitrate, of any strength, without causing copper to be deposited on the iron, while pieces from a batch of iron which rusts always cause the deposition of copper from the same solutions of copper salts. Sometimes the copper is deposited quickly, whilst at other times several hours may elapse before the deposition of copper takes place. The metal is always attacked at one or more points, and the deposition of copper spreads from these points over the whole surface in a very short time.

It is clear from these experiments that physical differences in iron of the same high state of chemical purity can cause most profound differences in its behaviour.

If the theory is true, we should expect such results. In the case of the iron which does not rust and is unaffected by solutions of copper sulphate or copper nitrate, the metal is probably physically homogeneous, at any rate on the surface. There would, therefore, be no differences of solution pressure—no electrically different parts—on the surface of the metal, and so no tendency for the metal to pass into solution by electrolytic action when the metal was put into an electrolyte. Since iron could not therefore pass into solution, we should not expect rusting to take

place, nor should we expect the deposition of copper on the iron from solutions of copper salts.

The processes preceding corrosion and the deposition of copper from copper salt solutions upon metallic iron are undoubtedly similar in character.

In the case of the samples of pure iron which rust and which cause the deposition of copper from solutions of copper salts, the metal, although chemically pure, is not physically homogeneous, owing probably to some inequality in the temperature of reduction or the rate of cooling.

If such be the case, differences of solution pressure would exist on the surface of the metal, and when it was put into an electrolyte there would be a tendency for electric currents to be set up between the electrically different points. In water, in the presence of air, this would lead to corrosion, in copper salt solutions to the deposition of copper. An interesting confirmation of such an argument is furnished by the following experiments:—

Some pieces of the pure metal were taken which had been exposed to the action of water and air for several months without showing any signs of corrosion. They were carefully dried between pure Swedish filter-paper, and then some of them were subjected to pressure in a polished agate mortar by an agate pestle, while others were left untouched. Some of the pressed pieces were then put in distilled water and exposed to the air; they rusted in the course of a few hours, rust forming first at the edges which had not been pressed by actual contact with the agate, whilst the pressed portions remained quite bright. Others of the pressed pieces were put into a solution of copper sulphate; copper was deposited immediately on the metal, deposition first commencing at the unpressed edges of the pieces.

The pieces of iron which had been dried but not pressed neither rusted when placed in contact with water and air again, nor did they cause copper to be deposited from copper sulphate solution, so that it was the application of pressure alone which caused the profound alteration in the properties of the iron.

This again is readily explained by the theory. If a piece of iron be originally homogeneous and part of it be subjected to a strain, then the piece will consist of two parts, a strained and an unstrained part—it will contain two different modifications of iron, each having a different solution pressure. If such a piece of iron be put in an electrolyte, there would now be a tendency for the passage of an electric current between the two electrically different parts, and so we should expect corrosion to take place when the iron was placed in contact with water and air. The fact that corrosion and the deposition of copper begin at the unpressed part shows that this part is relatively electropositive to the pressed part.

These same points are illustrated in a striking and very beautiful manner by the use of the ferroxyl reagent described by Cushman and Gardner ("Corrosion and Preservation of Iron and Steel," p. 48). The pure iron which does not rust is unaffected by the ferroxyl reagent, whilst the pure iron which is not physically homogeneous, or has been subjected to pressure, causes the development of the beautiful colours which indicate electrical differences, or differences of solution pressure, on the surface of the metal.

There are, however, some properties of pure iron which could not be predicted from the theory, but which cannot be considered as arguments against it.

The behaviour of pure iron towards solutions of copper chloride is altogether different from its behaviour towards solutions of the sulphate and the nitrate. Pure iron which has remained uncorroded after many months in contact with water and air, or which has remained unaltered in solutions of any strength of the sulphate or nitrate of copper, causes the immediate deposition of copper when placed in a solution of copper chloride, even when the solution is very dilute. The same effect is produced if sodium chloride is added to copper sulphate or nitrate solutions in which the iron has remained unaffected for long periods. The experiment is very striking if carried out in the absence of air. The iron quickly disappears, leaving behind finely divided copper, which in the course of a few hours is itself converted into white insoluble cuprous chloride.

Further, if a tube be taken containing pure iron which has remained unaltered in copper sulphate solution for a long period, and the temperature of the tube be raised to 100° C., copper is deposited on the iron, and in a short time all the iron passes into solution, leaving behind small crystals of copper.

These facts led the writer to suspect that the pure iron might conceivably be covered with a thin coherent film of some protective substance, and most careful experiments were carried out to test this possibility. It was finally decided, as the result of these experiments (*loc. cit.*) that this curious behaviour could not be accounted for by the presence of a protective film of either oxide or hydride on the iron.

The curious behaviour of the pure iron towards copper chloride solutions is interesting if considered in connection with the behaviour of the metal in sodium chloride solution. Even very dilute solutions of the chlorides of the alkali metals have a remarkable action in starting the corrosion of pure iron which has withstood the action of water and air for long periods without showing any signs of corrosion. The action of salt solutions on pure iron is at present under investigation, and the results are not ready for publication.

It is well known that ordinary commercial iron is rendered passive by certain substances, *e.g.*, nitric acid, solutions of caustic alkalis, or chromic acid, and that such passive iron, so long as the passivity persists, will not rust in contact with pure water and pure oxygen, and will not cause the deposition of copper from very dilute solutions of copper sulphate.

In view of what has been said above, it seems probable that these substances have the power, in some way or other, of altering the surface of commercial iron so as to destroy, temporarily, the electrical differences on its surface—to produce what might be described as an "electrically equable" surface. The result of this would be that the iron would possess no tendency to go into solution in an electrolyte, and so would not rust when placed in contact with air and water.

Much the same sort of "electrically equable" surface is produced in a plate of impure zinc when it is amalgamated.

Since passivity can be produced by such widely different substances, it is not improbable that the "electrically equable" surface produced is not always of the same nature.

The writer is inclined to the view, which is as yet unsupported by experimental evidence, that substances which protect iron from corrosion have the power, in some way or other, of destroying or reducing the electrical differences which always exist in commercial forms of iron—that they have a passiviving effect—and that the substances, like the chlorides of the alkali metals, which stimulate corrosion do so by increasing these electrical differences. This would explain the remarkable behaviour of pure iron towards copper chloride and alkali chloride solutions. For the present, however, the subject must be left open.

Fractional Distillation of Oil.—Léo Vignon.—When the results of the distillation of oils are studied from the point of view of the liberation of gases from them it is found that all the unsaturated hydrocarbons pass over below 600°. Methanes and saturated hydrocarbons are very abundant up to 800°; the proportion of them rapidly decreases as the temperature rises. Hydrogen predominates from 800° to 1000°. As much as 30 per cent of CO may pass over above 1000°.—*Bull. Soc. Chim. de France*, xiii.-xiv., No. 3.

COBALT DRIERS.*

By V. P. KRAUSS.

The cobalt compounds which are generally offered on the market to-day may be divided into two classes:—In the first are cobaltous oxide, acetate, sulphate, chloride, nitrate, hydroxide, and basic carbonate. In the second class are various grades and qualities of resinates (sometimes called sylvinates), both fused and precipitated, oleates or linoleates, oleo-resinates, tungates and resino tungates, besides some other liquid preparations composed in whole or part of the foregoing.

From the varnish manufacturer's standpoint the substances in the first division are crude materials which are utilised in the production of the compounds in the second class, and also in the preparation of some varnishes, liquid driers, drying oils, and the so-called paint oils. The materials enumerated under the second class are the result of a varnish maker's labour, and when properly made and used in mixtures to which they are adapted give very good results.

The inorganic salts of cobalt do not directly come under the scope of this paper, and thus will not be directly considered except inasmuch as their use as crude material affects the driers into whose composition they enter.

It is only within the past year that the cobalt driers have been offered to the American paint and varnish manufacturers. Up to the present time their use is not general, first, because of the very high price, and second because their use is not thoroughly understood and many experimenters have had unsatisfactory results and therefore refused to further consider the introduction of the new material. Furthermore, not all of the cobalt driers, whether liquid, paste, or solid, now offered for sale, are properly made and truly adapted to the purposes for which they are recommended. This situation in addition to unsatisfactory results obtained by some of those experimenting, would naturally have a retarding effect on the introduction of a new type of material.

The salts of cobalt which are at our disposal in commercial quantities, are all of the cobaltous or divalent type. It has been found that although they can be readily used in the manufacture of driers and worked like the various compounds of manganese, lead, zinc, calcium, aluminium, &c., the organic compounds formed, which are the basis and active principles of the so-called driers, are not efficient while in the cobaltous state. The cobaltic combinations, however, are very active driers, and it is for the formation of trivalent cobalt compounds that we strive in the making of driers. This transformation can be effected in several ways. By blowing cold, heated, or ozonised air through the hot cobaltous drier stock, or by the introduction of liquid or solid oxidising agents. The use of cold or even heated air is a very long and tedious operation if carried out to the extent to which it is necessary in order to get the maximum strength in the drier, and greatly adds to the cost of an already expensive material. The use of the liquid or solid oxidisers can be carried out successfully and in a comparatively short time, although even when great care is exercised the batch of material is in danger of catching fire.

Since driers are used in a number of industries in which drying oils form part of the material produced, and since the operating methods of the various manufacturers are widely divergent, the siccatives or driers adapted to each will in many instances show widely different characteristics, not merely in form but also in composition.

Since the paint manufacturer and also the practical painter who mixes his own paints from paste colours and raw or treated oil, are the principal consumers of what are generally known as driers, the materials adapted for their use may be first considered. The driers will, in practically all instances, be in the liquid state, either very fluid, of heavy consistency or of a semi-paste nature. In composition, they will mostly consist of resinates, tungates, oleates, or linoleates, or combinations of the three. For the drying of linseed oil, when the proper driers are selected, little or nothing can be asked in addition to those known at present. When the general lead, manganese, and other prevalent metallic driers are well chosen, raw linseed oil can without any difficulty be made to dry by the addition of from 5 to 10 per cent or even less, the time of drying under average weather conditions being from 10 to 24 hours. By the use of cobalt driers, the same drying effect can be obtained when only from 1 to 3 per cent of a liquid drier is used. I am not yet prepared to say positively what the ultimate effect of cobalt driers is upon paint films, but from my experiments I am led to believe that cobalt has not the harmful progressive oxidising action that some of the usual manganese lead compounds have. It has also been noticed that although a cobalt drier may be fairly dark in colour, it will not have as darkening an effect as one of the usual driers of like colour would have upon a white paint. The cobalt driers likewise show the same phenomena as some of the others when used in excessive amount; that is, although the paint film will set up well in the usual time, the drying action apparently reverses and the film remains tacky.

The terms applied to liquid driers are often uncertain and apt to be misleading. There are no general standards for strength or consistency, and, it must be admitted, many of the materials found on the market contain more volatile thinners than is conducive to obtaining a maximum drying effect with a minimum quantity of drier.

The value of the cobalt specialties depends not on their power to dry linseed oil, but on their ability to make the lower priced semi-drying oils act like it.

Soya, fish, and even corn and cottonseed oil are adaptable for use in paint, and when correctly treated increase its durability. Dr. Maximilian Toch has published the results of his extensive research and experimental work with both fish and soya oils, and there describes the types of driers suitable for them.

In the making of waterproof fabrics, insulating coatings, &c., both liquid and solid driers are used. In the linoleum, oilcloth, patent leather, artificial leather, and similar industries, the semi-liquid, paste, and solid driers are in demand, since for these products the manufacturers cook the oils and varnishes in their own factories.

The paste and solid driers must essentially be considered under the caption of crude materials because they must be churned or cooked in the oils or varnishes in which they are used.

The methods of making both solid and liquid driers are in general similar in the first stage of the process, and thus may be described under the same headings.

Resinate of Cobalt, Precipitated and Fused.

This is correctly made by saponifving rosin or colophony with caustic soda or sodium carbonate, care being taken to avoid an excess of the reagent, and then precipitating with a solution of some salt of cobalt. The chloride or sulphate serve best for this purpose. The precipitated resinate, or as it is sometimes called, rosinate or sylvinate, must then be thoroughly washed and then pressed and dried. This will yield a pinkish, fairly fluffy powder when ground, which will readily dissolve in oil at a low temperature. The fused variety is made by melting the dried resinate in a kettle and then pouring into cooling pans. The operation is performed more rapidly by taking the cakes from the presses and driving off the water and fusing in one operation.

Cobalt Oleates or Linoleates.

The basis of this class is generally linseed oil, although walnut, perilla, soya, and some other oils may be used. The oil is thoroughly saponified with caustic soda and

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like the resinate, precipitated with a salt of cobalt. The material is then carefully washed and pressed. It may be melted to form a dark viscous heavy fluid.

Several samples of cobalt linoleate which I examined consisted of bodied linseed in which small amounts of inorganic cobalt salts had been dissolved. Another was of the same order with the addition of volatile solvents.

True linoleate of cobalt, when fused with varnish gums and dissolved in volatile oils, yields an excellent drier.

Oleo-Resinates.

This type of drier is made by melting together the precipitated resinate and linoleate, sometimes with the further addition of fused fossil gum-resins.

Tungate of Cobalt.

Like the linoleates, the tungate of cobalt is made by saponifying pure China wood oil (tung oil) with caustic soda, care being taken to avoid excess of caustic, and then precipitating with a salt of cobalt. The tungate is then washed thoroughly, pressed, and generally dried and fused. Great care is necessary in the preparation of a tungate since it oxidises very rapidly, and the oxidised material is useless.

Like the linoleate of cobalt, the tungate may be fused with the resinate to form what may be called a resino-tungate.

In general, the foregoing substances are incorporated in oils by means of heat. the combining temperature being between 300° and 500° F. The amount necessary will vary from about ½ per cent to 5 per cent. In order to make *liquid driers*. the paste or solid driers can be melted alone or in combination with gum-resins, bodied linseed oil, or both, and then thinned to liquid consistency with volatile oils.

Among other cobalt salts, some of the chemical manufacturers offer the acetate, with directions for its use as a drier. All agree that between two- and four-tenths of 1 per cent are necessary to dry linseed oil. The oil should be at a temperature between 300° and 400° F., and be carefully stirred until all the salt is dissolved. Soya and China wood oil may be similarly manipulated.

It is still a little too soon to make a positive statement as to how oils thus treated with the acetate withstand wear and exposure.

Cobalt oxide, like the acetate, can be directly added to il during boiling. It however dissolves slowly and necessitates heating to high temperature; the resulting product is also very dark. and mostly consists only of bodied oil. Rosin also will directly combine with cobalt compounds on heating together in a suitable kettle or container. The product possesses a number of objectionable features. It still is mostly unchanged rosin, has become much darker and lost considerably in weight due to volatilisation. I have tried the effect on oils of quite a number of cobalt compounds, but found none equal in efficiency to those described in the foregoing.

Rôle of Sulphate of Barium and Calcium in the Reduction of Zinc Ores.—Eug. Prost and Maurice Ubaghs.—Lime is a regular constituent of blendes, in proportions ranging from 1 to 5 per cent. Barium carbonate and sulphate are also frequently present in them. When blendes are roasted most of the barium and calcium are converted into sulphate, and in presence of silica these sulphates may hinder the reduction of zinc ores. They consume a certain amount of heat for their decomposition or reduction, and also they tend to regenerate zinc sulphide, which remains in the residues of distillation and thus increases the loss of zinc, or else is reduced only at a very high temperature, to reach which entails waste of fuel.

THE TESTING OF SAFETY EXPLOSIVES.*

By Prof. VIVIAN B. LEWES, F.I.C., F.C.S., &c.

THIRTY years ago the so-called safety explosive was practically unknown, and gunpowder was the chief agent used by the miner both for coal and quarry work, whilst where greater power was needed dynamite was employed. The danger of these explosives in dusty or gassy mines being realised in the early eighties, attempts were made to introduce explosives giving less flame, and therefore less chance of firing the mixture of air and inflammable matter in the event of a blown-out shot, and in 1883 Favier, in France, introduced an explosive of the same character as ammonite, whilst roburite was patented in 1887. In the meantime many successful explosives containing nitroglycerin, cooled down during explosion by admixture with other ingredients, had been introduced, and by 1890 the list of safety explosives had attained considerable dimensions; but in the early days of the industry the chief tests applied to them were with the view of determining their safety in handling and transit, and the chief point which had to be attained was insensitiveness to ordinary shock or friction. In 1896, however, the requirements of the Coal Mines Regulation Act led to the erection of a testing gallery at Woolwich, copied from one that had been fitted up by the Institute of Mining Engineers in Northumberland, in which the liability of the explosives to ignite mixtures of coal-gas and air could be determined, whilst their relative strength could be ascertained by firing into the ballistic pendulum.

As far as I know, at the time the testing gallery at Woolwich was introduced the only Continental installation of the kind was the gallery at Gelsenkirschen, where, under auspices of Dr. Beyling, much good work was done; but later several other private testing galleries were set up, and the French, Austrian, Belgian, and American testing stations were erected.

There were, however, great differences between the methods of procedure adopted, the chief being that in the Continental practice the explosives were fired unstemmed into the test mixtures, or even suspended in them, whilst at Woolwich stemming was used.

For some time prior to 1912 vague rumours had been afloat amongst the manufacturers of safety explosives that alterations of a far-reaching character were about to be introduced in the official testing of explosives for inclusion in the permitted list, that the testing station was no longer to be at Woolwich, but was to be moved to the coal-fields, and that the tests were to be made so severe that only the best on the existing list would be likely to survive them. These rumours were confirmed by the issue in May, 1912, of a Home Office Memorandum, revising the test of explosives for inclusion in the permitted list after March 31 of this year.

The cause of this alteration is a praiseworthy desire on the part of the Home Office authorities, not only to bring our method of testing into line with that adopted by other countries, but also to render the explosives permitted for use so absolutely safe as to eliminate practically all danger from them in gassy and dusty mines, and as blown-out shots have proved the most frequent cause of ignition of gas or dust, they have adopted the procedure for the Rotherham tests of doing away with the tamping used in the Woolwich mortar, and of firing the charge direct into an explosive mixture of lighting-gas and air, and also into finely-divided coal-dust suspended in air. the largest charge which fails to ignite either mixture over a series of five shots being known as the "maximum charge," and this must not be less than 8 ozs. (226·8 grms.).

There is not the least doubt that this is a test so severe that very few of the explosives up to the present on the permitted list will pass it, and inasmuch as some have proved absolutely safe in practical working, it will be well

* A Paper read before the Royal Society of Arts, April 2, 1913.

to examine how far the new procedure really does attain the object in view, and whether in attempting to gain perfect safety the authorities are not running the risk of opening the door to still greater danger than now exists. It is no use advancing such criticisms as are brought forward, mostly by those whose trade interests have been affected, such as :—" It is criminal for an unstemmed shot to be fired in a mine, and therefore absurd to introduce it in a test," or " The new regulations are framed to save the life of the test cannon and not that of the miner," &c. The plain answer to all such is that the authorities are wholeheartedly anxious to fulfil the duties for which they were appointed, and that such tests are carried out at Frameries and elsewhere, and that unless it can be shown that the drawbacks, from a purely scientific and practical point of view, are greater than the advantages, the new regulations must stand until a better method of testing has been devised.

These are the only lines on which criticism could be considered, and this paper is merely an attempt to show some points to which attention might be directed, rather with the view of perfecting the present regulations than of opposing them.

The whole question is one of the greatest complexity, and a true solution of it requires consideration of every factor entering into it.

At the outset it will be of interest to recall the inception of the " unstemmed " test, and to note that it originated, not with Government officials desirous of shelving responsibility for any accidents due to permitted explosives, but with the mine-owners themselves.

The law in Germany is that only " safety explosives " shall be used in mines liable to gas or dust, and leaves the onus of finding out what a "safety explosive " is to the mine-owner ; in this way not only ridding the Government of responsibility, but ensuring the best expert knowledge being applied to solving the problem. The outcome of this was the erection of the Gelsenkirschen testing station, and at a later date the one at Grube Maria, both of which are under the auspices of the Berggewerkschaftskarse.

It was soon realised that safety with an explosive is purely a relative term, and that, as it was impossible to reproduce in testing all the varied conditions of practical work in a mine, it was better to apply as stringent a test as possible, so as to select the safest explosives from amongst the host that had sprung up ; and so, at the initiative of the mine-owners, the German practice arose of firing the explosive untamped into the gas mixture, whilst in the Austrian tests it was simply fired suspended in the mixture.

In 1903 M. Watteyne, who was in charge of the then newly erected Belgian official testing station at Frameries, suggested at the International Congress of Applied Chemistry at Berlin, that as every explosive when fired untamped into the test mixture of gas and air would cause ignition if the charge were only large enough, the largest charge which in a given number of shots failed to ignite the mixture should be called the *charge limite*. This idea met with general approval, as it afforded a method for arranging the explosives in order of danger, and although it by no means followed that when used in practice, that is to say, tamped, an explosive which failed to pass the test would lead to trouble in the mine, yet it did seem certain that one that passed the test with a high *charge limite* would not only be safer, but that if the *charge limite* was not exceeded even a blown-out shot in a gassy mine would not be likely to cause a disaster.

In nearly all the early tests made to establish the *charge limite* on the Continent, coal-dust was used suspended in the gaseous test mixture, but it was soon found that, contrary to expectation, it did not increase the sensitiveness of the mixture to explosion, and that a mixture of coal-dust and air alone was often more sensitive than when gas was present. The reason of this was not understood at the time, although Dr. Harger's work has now made the cause clear, but the fact that it was so led to the introduction of the method of using two test mixtures—the one an explosive mixture of pit-gas, coal-gas, artificial methane or benzene vapour with air, and the second a mixture of coal dust and air, the *charge limite* of an explosive being the largest charge that in a definite number of shots failed to ignite either mixture. This procedure was adopted at Frameries, and at the International Congress of Applied Chemistry, held in London in 1909, M. Watteyne communicated the results obtained by M. Bolle in re-testing the explosives already on the Belgian permitted list for gassy mines.

Attractive as was the idea of being able to fix a definite ratio of danger in the explosives, it was impossible to introduce the *charge limite* into England with the apparatus in use at Woolwich, as the gallery being only 2 ft. 6 ins. in diameter the explosives could not be fired unstemmed, as a few grms. would have ignited the mixture, whilst they could not be fired in sufficient quantities if stemmed without destroying the test cannon. When, however, circumstances arose that necessitated the removal from Woolwich and re-modelling of the test apparatus, it was decided that the Continental practice should be adopted, and explosives for the permitted list should pass the tests with a " maximum charge " of not less than 8 ozs.

When this method of testing became general on the Continent, it was at once found that, although the results given at each individual gallery were fairly concordant, no two galleries agreed in the weight of the maximum charge assigned to various explosives, and that although the order of safety—or, if it be preferred, the degree of danger—was much the same, yet the conditions at some testing stations were so much more sensitive than at others that the *charge limite* at one might vary by 50 per cent from that fixed at another. Experiments soon showed that these variations were due to a large number of factors, some of which may not be known even yet, and that the shape and section of the gallery, the dimensions of the bore of the gun, the percentage and character of the gas used for making the mixture, the warming of the gallery by sun, the composition, size, and freshness of the coal-dust used, and even the atmospheric conditions, were all factors, apart from the explosive itself, that influenced the results obtained.

The testing station at Frameries is under exactly the same official conditions as the new station at Rotherham, explosives being submitted for test by the manufacturers, and the composition, strength, and *charge limite* of those that pass the test being published in the official reports, and so much valuable experimental work has been done and published by M. Watteyne and his able staff that it will be well to see in what respects the Rotherham procedure differs from the Frameries tests, and how far the results obtained from the latter can be taken as an indication of the probable results found at Rotherham. The dimensions of the testing gallery and bore of the cannon at the two stations are as follows :—

Gallery.	Frameries.	Rotherham.
Sectional area ..	2 sq. metres ..	1·8 sq. metres (5 ft. diam.)
Length	30 metres	15·2 metres (50 ft.)
Material	Wood	Iron
Cannon.		
Length of bore ..	46 cm. = 1·5 ft...	4 ft. = 120 cm.
Diameter	5·5 cm. = 2 ins...	2 ins. = 5·5 cm.

Much valuable work has been done on the effect of the diameter of the gallery, and its sectional area on the sensitiveness of explosive mixtures, and the general view at first taken was that approximately it varied inversely with the sectional area—that is, a gallery of 1 sq. metre section was twice as sensitive as one of 2 sq. metres section. It is clear, however, that although this might be so, if the prevention of ignition of the test mixtures depended entirely upon the cooling of the products of com-

bustion by expansion, yet as the nature of the products must play a very important part in the effect produced, the influence of the size of the gallery will depend largely upon the kind of explosive used.

MM. Watteyne and Bolle at Frameries tried the effect of the area of the gallery, and found that the maximum charge was reduced very largely with some explosives and but little affected with others. They used galleries having roughly the area of 2 sq. metres, 1 sq. metre, and ½ sq. metre. They experimented with several representatives of the chief classes of safety explosives, and found that a "wetter dynamite" showed no reduction in the maximum charge in dust with decrease in the size of the gallery, whilst under the same conditions a carbonite gave the greatest reduction. On the other hand, the wetter dynamite had its maximum charge reduced to one-half in gas, whilst the carbonite was reduced only by 28 per cent in the smallest gallery. The figures obtained are of considerable interest:—

	Fire-damp mixture.			Coal-dust mixture.		
Area, sq. metre ..	0·28	0·95	2	0·28	0·95	2
	Relative charge limit					
Class.						
Wetter dynamite..	0·46	0·46	1	1	1	1
Carbonite	0·72	0·94	1	0·06	0·28	1

The difference is caused by the fact that the products of combustion of the wetter dynamite contain 45 per cent of water-vapour, which is very effectual in preventing the ignition of coal-dust, whilst the products of the carbonite contain only 7 per cent of water-vapour, giving probably less than any other explosive.

It is clear from these experiments that the check on the free expansion of the products of combustion by diminution in the area of the gallery does not affect all classes of explosives alike, and that although in erecting the Rotherham gallery it was a pity for the sake of uniformity that the 2 sq. metre area was not adhered to, yet even if the old idea as to the effect of area had been correct, it would have been only 10 per cent more sensitive than the Frameries gallery.

Turning now to the cannon and the influence which the dimensions of the bore have upon the tests, we find that at Rotherham the bore of the cannon is 4 ft. long by 2 ins. in diameter, and the cartridges supplied have to be 1⅞ in. in diameter with an allowance of $\frac{1}{16}$ in.—that is to say, the cartridge will occupy half the sectional area of the bore. It is clear that an unstemmed shot under these conditions in no way represents a blown-out shot in practice. Beyling has pointed out that with a mortar having a bore of 2⅛ ins.. *i.e.*, ⅛ in. larger than the Rotherham cannon, an explosive of the class that gives off carbon monoxide on explosion, done up in 1⅞ in. cartridges, would pass the test of firing unstemmed with a *charge limite* of 1000 grms., because the products expanded in the bore are cooled to such an extent that when discharged into the mixtures neither gas nor dust is ignited, but that when the cartridges were fired in a narrow-bore cannon (1·57 in.), which they nearly fitted, 735 grms. ignited gas and 130 grms. ignited dust, because the carbon monoxide is blown out at a temperature high enough to ignite on coming in contact with air, and then ignites the dust.

That is to say, an explosive which would possibly pass the highest class at Rotherham might, with a blown-out shot in practice, with cartridges fitting the bore, give an explosion in a dusty mine with a charge of 130 grms.

This is a real danger, and one to which I shall allude again in dealing with the class of explosives that give large volumes of products of incomplete combustion.

It will be noticed that the bore of the Rotherham cannon is much longer than of those employed at Frameries, and it seems probable that this must give rise to differences, as it has been shown that increase in the length of the bore increases the length of the flash from the cannon, and at any rate suggests two other objections acting in the opposite direction, the first being that the great mass of metal conducts the heat away rapidly from the products of combustion, and the second is that this factor increases with increase in the factor of danger, as, with an explosive which will pass only with a maximum charge of 8 ozs., the cartridge occupies only the bottom 7 or 8 ins. of the bore, and has over 3 ft. of cold metal surface to cool the products before they reach the test mixtures, whilst an explosive that has a big maximum charge nearly fills the cannon, and the top of the charge and detonator fire direct into the mixture without the cooling help of the metallic contact, so that, to a certain extent, the dangerous explosive is favoured and the safe one penalised.

We will now pass to the test mixtures, which consist of:—

1. A mixture of 55 cubic feet of Rotherham coal-gas with 299 cubic feet of air, filling the 354 cubic feet of space at the end of the gallery into which the shot is fired, and being retained there by a paper diaphragm, is equivalent to 15·5 per cent of gas on the capacity of the chamber, but is reduced to about 13·5 per cent by air in tubes, &c.
2. 120 ozs. of coal-dust, 40 ozs. of which are arranged on a board in the first 10 ft. in front of the mouth of the cannon, whilst the remaining 80 ozs. are placed in heaps in the remaining 40 ft., so that when the shot is fired the rush of the products of combustion stirs up the dust cloud.

When the testing gallery was removed from Woolwich, it was generally supposed that the Midlands had been fixed upon as yielding a supply of pit-gas for the test, but the authorities came to the conclusion that the supply of coal-gas would be of more even composition than a natural gas, and that as there was only some 50° C. difference between their recorded ignition points, it was better to adopt coal-gas for making the mixture. If the Rotherham test is accepted as a purely empirical test intended to place explosives in their order of danger, this conclusion is justified; but if there was any intention of making the tests resemble practical conditions, it was a mistake, as there is one point about the ignition of pit-gas on which I do not think sufficient stress is ever laid. In the beautiful work of Dixon and Coward on the ignition points of gases, the determination was made by heating both gas and air before they came in contact, and noting the temperature at which ignition of the gas took place on coming in contact with the air. In a large number of experiments the ignition point of hydrogen varied only between 580° and 590° C., whilst with methane and air the variations were from 650° to 750° C., *i.e.*, ten times as great. The cause of this is that the hydrogen unites directly with the oxygen of the air, forming water-vapour, whilst, as Bone and Wheeler have shown, when methane burns with oxygen, formaldehyde is produced first and then breaks down to carbon dioxide and water, and the time necessary to complete this reaction gives what has been called "retarded ignition." The French Explosives Committee many years ago adopted 650° C. as the ignition temperature of pit-gas, but found that this temperature had to be applied for ten seconds before the gas ignited, whilst for its immediate ignition a far higher temperature had to be applied. It is this which causes the danger with gunpowder and other slow-burning explosives, which, in the event of a blown-out shot, would give a flame of long duration, whilst with more rapid explosives, which on detonation give a flash lasting only for the fraction of a second, the flash or the products have to come in contact with the fire-damp whilst still at a very high temperature to cause ignition. With Rotherham coal-gas, however, which contains approximately half its volume of hydrogen, the temperature would have to be considerably less than that needed for fire-damp to give immediate ignition, so that a flash from an explosive having a temperature far too low to ignite a pit gas mixture would easily ignite the coal-gas mixture.

(To be continued).

PROCEEDINGS OF SOCIETIES.

SOCIETY OF CHEMICAL INDUSTRY.

(London Section).

Ordinary Meeting, April 7th, 1913.

Prof. W. R. Hodgkinson in the Chair.

The following paper was read and discussed:—

"*High Pressure Reactions: The Formation of Coal and of Hydrogen.*" By Dr. F. Bergius, of Hanover.

The author, after alluding to the work of Haber and Le Rossignol, and to his own work on the oxidation of calcium oxide to peroxide under high pressure, briefly described the preparation of hydrogen of 99·95 per cent purity by the action of iron on liquid water at high temperatures and pressures. It was shown that the presence of electrolytes increased the velocity of the reaction which was not merely superficial, as the iron was oxidised throughout to Fe_3O_4. The operation had been carried out on a large scale.

The author also referred to the carrying out of exothermic reactions under regulation, such as the decomposition of pure cellulose and of peat. By heating such substances under pressure at 340° C. for eight to sixty-one hours, a substance resembling soft coal was produced, together with carbon dioxide and water. The author calculated, from the rate of production of this substance, that about eight million years would be required, under the probable conditions of formation of coal in nature, for the production of a coal of similar composition.

The substance possessing the chemical properties of coal can be made to acquire its physical properties by further great compression. At extremely high pressures a substance of high carbon content and possessing the physical properties of anthracite is produced.

The author described reaction vessels and cone joints, by the aid of which he could maintain very high pressures for prolonged periods.

NOTICES OF BOOKS.

The Laboratory Book of Dairy Analysis. By H. Droop Richmond, F.I.C. Second Edition. London: Charles Griffin and Co., Ltd. 1912.

In preparing a second edition of this useful summary of methods of analysing dairy products the author has made a few corrections and alterations. The new methods described include the "Sinacid," "Sal," and "Neusal" methods of estimating fat in milk, and the determination of the aldehyde figure. The Avé-Lallemant process for analysing butter and the Hinks method of detecting cocoa-nut oil in butter are also given.

The Organometallic Compounds of Zinc and Magnesium. By Henry Wren, M.A., D.Sc., Ph.D. London: Gurney and Jackson. 1913.

Advanced students and those engaged in research will find this monograph useful as a guide to and summary of the very great number of articles and papers which have been published on the magnesium and zinc organic compounds. The reaction first studied in detail by Grignard, and known by his name, is employed in many syntheses, and plays an increasingly important *rôle* in organic research. Details of the preparation and experimental use of the reagent are given in the first section, and in Part II. the various products obtained by its use are discussed. These include both organic compounds of all classes and some miscellaneous inorganic products, as well as silicon compounds. In the section on theoretical considerations various theories which have been put forward as to the actual constitution of the reagent are summarised, much attention being paid to Tschelinzeff's work. The organic derivatives of zinc, less active and less widely used than the corresponding magnesium compounds, are discussed in the last section.

Scientific Papers. By J. Y. Buchanan, M.A., F.R.S. Volume I. Cambridge: The University Press. 1913.

This volume contains the author's papers on "Oceanography," describing his work as physicist and chemist to the *Challenger* Expedition, and later on the s.s. *Buccaneer*. The papers, many of which appeared in the *Proceedings* of the Royal Society, are reprinted exactly as they were first published. They will be read with interest by men who are engaged in similar work, though in all directions very great advances have been made since they were written in our knowledge of the subjects of which they treat.

CORRESPONDENCE.

THE INFLUENCE OF LEAD ON THE FERROCYANIDE TITRATION OF ZINC.

To the Editor of the Chemical News.

Sir,—I beg to call attention to the method used by Victor Lenher and C. C. Meloche for the estimation of zinc in ores by the ferrocyanide method (Chemical News, cvii., 161). They state that it is unnecessary to remove lead. I wish to point out the fact that by this method lead is unavoidably removed; its influence, therefore, upon the titration of the zinc is of no consequence. When the ore is dissolved in hydrochloric acid and the resulting solution diluted, the bulk of the lead separates as chloride and remains in the insoluble matter, and with care as to temperature of removal it can be made complete enough to allow of its estimation. In the absence of this precaution a small quantity of the lead remains in solution, but is afterwards separated as hydroxide along with the iron on addition of ammonium hydroxide.

I have had occasion to investigate several methods for the estimation of zinc in oxides containing both lead and iron, and have come to the conclusion that the ferrocyanide method is the best when carried out carefully.

The following, in my opinion, are the three main points to be observed for the successful manipulation of the titration:—(1) Oxidising agents should be absent, as their presence almost invariably produces high results, owing probably to a little ferrocyanide being oxidised to ferricyanide, this ferricyanide then not taking part in the chemical reaction. The best oxidising agent for the iron is hydrogen peroxide, as the excess can afterwards be decomposed by boiling; (2) the solution should be titrated at 100° C., and should not be allowed to fall below 80° C. during the titration; (3) the excess of hydrochloric acid should not be added until the solution has been removed from the hot plate or burner and is quite ready for the titration, as a boiling solution of zinc chloride tends to decompose hydrochloric acid with the liberation of chlorine, which oxidises the ferrocyanide on commencing the titration.

The best indicator, I think, is a strong solution of uranium acetate, and it can be used both internally and externally.—I am, &c.,

H. Williams.

1, Rockingham Terrace,
Borough Road (East), Middlesbrough,
April 5, 1913.

Royal Institution.—A General Meeting of the Members of the Royal Institution was held on the 7th inst., Sir James Crichton-Browne, Treasurer and Vice-President, in the Chair. Mr. Walter L. Allcroft; Sir Robert Filmer, Bart., J.P.; Prof. A. Schuster, Sec. R.S.; and Colonel A. L. M. Turner, R.A.; were elected Members.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xlvi., No. 2, 1913.

Lecture Experiments with Diamonds.—Wilhelm Prandlt.—Moissan's experiment may be repeated as follows:—A mixture of commercial iron thermite and powdered carbon is placed in an iron plate cylinder packed with fluor-spar. The thermite mixture is ignited, when it melts through the cylinder, and is allowed to fall into water. The granulated iron and the slack can easily be separated mechanically. To isolate the "diamonds" the iron is treated with HCl and aqua regia. The residue is oxidised with potassium chlorate and nitric acid, the insoluble part is evaporated with a mixture of hydrofluoric acid, sulphuric acid, and nitric acid, and then fused with sodium bisulphate. The powder finally remaining is washed and dried, and taken up with methylene iodide. The particles which sink to the bottom contain diamonds. Diamonds can readily be burnt in a quartz tube to which is connected a washing flask containing lime or baryta water. When a current of oxygen is led in and a temperature of 850° is reached the formation of carbon dioxide is observed.

Triphenylmethyl Oxide.—M. Gomberg.—Triphenylmethyl derivatives are oxidised normally by means of mercury oxide, giving triphenylmethyl oxide almost quantitatively. Moreover, when triphenylmethyl carbonate (m. p. 205—210°) is heated to 140° in the presence of copper as a catalyst it decomposes into the oxide and carbon dioxide—

$$(C_6H_5)_3C.O.CO.O(C_6H_5)_3 \rightarrow CO_2 + (C_6H_5)_3C.O.C.(C_6H_5)_3.$$

New Reaction for Elementary Oxygen.—Karl Binder and R. F. Weinland.—A deep red solution is obtained when alkalis are added to a solution of pyrocatechin and ferric salt. The colour is due to the formation of a compound of formula $[Fe(C_6H_4O_2)_3]K_3$. In presence of free oxygen the same compound is obtained from a ferrous salt—

$$2FeSO_4 + 6C_6H_4(OH)_2 + 10KOH + O = 2[Fe(C_6H_4O_2)_3]K_3 + 2K_2SO_4 + 11H_2O,$$

and this reaction can be employed for the detection of free oxygen and also for its quantitative estimation.

Atti della Reale Accademia dei Lincei.
Vol. xxi., [ii.], No. 12, 1913.

Existence of Natural Ozonised Waters.—R. Nasini and C. Porlezza.—The authors have proved that natural waters occur which are permanently and normally ozonised. Some which are rich in ozone smell distinctly of it. The phenomenon of the existence of such ozonised waters may be explained by supposing that the formation of the ozone is due to the autoxidation of ferrous bicarbonate.

Sulphoaluminates of Silver.—Livio Cambi.—Sulphoaluminates of silver can be prepared by the sulphation of mixtures of silver and aluminium at 900—1200°, using pure dry sulphuretted hydrogen. Thermic analysis shows the existence of a compound containing about 43 per cent Al_2S_3, and corresponding to the formula $4Ag_2S.5Al_2S_3$. It fuses unaltered at 1035°. In all probability another compound, which decomposes at 825°, exists; it contains 70 to 60 molecules per cent of silver sulphide ($2Ag_2S.Al_2S_3$?).

Vol. xxii., [i.], No. 1, 1913.

Use of Cupferron in Quantitative Analysis.—I. Bellucci and L. Grassi.—Baudisch has recommended the use of the ammonium salt of nitrosophenylhydroxylamine, $C_6H_5.(NO).N.ONH_4$ ("cupferron"), for the estimation of copper and iron. The authors, having occasion to determine the composition of alloys of titanium and aluminium (obtained by reducing potassium fluotitanate with excess of aluminium), have investigated the use of the same reagent for the purpose. A solution of cupferron, added to an acid solution of titanium chloride or sulphate, gives a precipitate of the normal salt of nitrosophenylhydroxylamine, and titanium can very accurately be determined in presence of aluminium by this reagent.

Action of Distilled Water on Impure Aluminium.—A. Scala.—When aluminium is exposed to the prolonged action of distilled water at a temperature of about 22—26° a certain amount of alumina is formed. At the same time a small quantity of a brown substance is formed. The author was unable to carry out a complete analysis of it, but it appears to be a compound of alumina, iron, and perhaps silicon. Hydrogen is also generated.

MISCELLANEOUS.

Iron and Steel Institute.—The Annual Meeting of the Institute will be held at the Institution of Mechanical Engineers, Storey's Gate, Westminster, on Thursday and Friday, May 1 and 2, 1913, commencing each day at 10.30 a.m.—The Autumn Meeting will be held at Brussels, from September 1 to 5. Further particulars of the arrangements and of the excursions after the Meeting will be announced in due course.—Members of the Iron and Steel Institute are invited, by the Executive Committee, to participate in the Twelfth International Congress of Geology, which will be held in Toronto from August 7 to 14, 1913. The subscription to the Congress is five dollars. Arrangements will be made for excursions, both before and after the Meeting, to various places of geological interest in Canada. Further information can be obtained on application to the Secretary, Mr. W. Stanley Lecky, A.R.S.M., Victoria Memorial Museum, Ottawa.—The Sixth International Congress of Mining, Metallurgy, Applied Mechanics, and Practical Geology will be held in London during the month of June, 1915, at a date to be announced later.—The Eighth Congress of the International Association for Testing Materials will be held at St. Petersburg, during the Summer of 1915, at a date which will be announced later.

MEETINGS FOR THE WEEK.

Monday, 21st.—Royal Society of Arts, 8. (Cantor Lecture). "Antiseptics and Disinfectants," by David Sommerville.

Tuesday, 22nd.—Royal Institution, 3. "The Heredity of Sex and some Cognate Problems," by Prof. William Bateson, F.R.S., &c.

Wednesday, 23rd.—Royal Society of Arts, 8. "The Design and Architectural Treatment of Shops," by H. V. Lanchester, F.R.I.B.A.

Thursday, 24th.—Royal Institution, 3. "The Progress of Hittite Studies—Religious Monuments of Asia Minor," by Prof. John Garstang, M.A., &c.

—— Royal Society. "Protostigmata in Ascidians" and "The Origin of the Ascidian Mouth," by A. G. Huntsman. "Experiments on the Kidneys of the Frog," by F. A. Bainbridge, S. H. Collins, and J. A. Menzies. "Probable Value to *B. coli* of 'Slime' Formation in Soils" and "Variation in *B. coli*—the Production of two Permanent Varieties from one Original Strain by means of Brilliant Green," by Cecil Revis.

—— Society of Dyers and Colourists, 8. "Chemistry of Vat Dyes," by E. de Barry Barnett, B.Sc.

Friday, 25th.—Royal Institution, 9. "Meroë, Four Years' Excavations of the Ancient Ethiopian Capital," by Prof. John Garstang, M.A., &c.

Saturday, 26th.—Royal Institution, 3. "Mediæval French Novelists," by Prof. Sir Walter Rayleigh, M.A.

THE CHEMICAL NEWS

VOL. CVII., No. 2787.

ATOMIC WEIGHT ESTIMATION FROM SPECIAL GROUPINGS OF THE HYDRIDES.

By F. H. LORING.

THE estimation of atomic weight by means of tabular schemes is well known, and a very high degree of perfection in this method was reached by Mendeléeff in his studies.

Since the radio-active elements have been discovered, many efforts have been made to arrange these more or less transient bodies in special periodic classifications.

With the advent of a more thorough chemical knowledge of the radio-active elements, several successful attempts have been published. A considerable number of papers on the valency and classification of these elements have appeared this year :—

G. v. Hevesy, *Phys. Zeit.*, xiv., 49 ; *Phil. Mag.*, xxv., 390 ; *Le Radium*, x., 65 ; *Zeit. Elektrochem*, xix., 291 ; K. Fajans, *Phys. Zeit.*, xiv., pp. 131, 136 ; *Le Radium*, x., pp. 61, 57 ; A. S. Russell, CHEMICAL NEWS, cvii., 49 ; F. Soddy, CHEMICAL NEWS, cvii., 97 ; *Nature*, xci., 57 ; *Jahrbuch d. Radioakt.*, x., 188 ; A. Schuster, *Nature*, xci., 30 ; N. R. Campbell ; *Nature*, xci., 85. Some of these papers cover the same ground.

In a few of these principal communications, which bear directly upon the valency and periodic classification of the radio-active elements, it may be of interest to observe that the atomic weight of actinium has been estimated at 226·5 (Fajans) and 230 (Soddy).

It may also be worth while noting that special classifications of the *hydrides* would seem to afford a means of fixing approximately certain atomic weights, in particular those of radium and actinium.

Unfortunately, however, just where the greatest assistance is needed in arriving at the magnitude, *two* assumptions have to be made ; first, that the element in question forms a hydride of a particular type ; and secondly, that the special arrangement is, in general, accurate or applicable.

Nevertheless, Tables I. and II. (diagram) may be of interest, notwithstanding their artificial nature. The fact that high authorities have agreed that the atomic weight of actinium is probably near to that of either radium or thorium is perhaps sufficient reason for venturing further in the direction of extrapolation than one would otherwise do.

Inasmuch as the tables are self-explanatory, no special comment need be made, except to call attention to the possibility that J. J. Thomson's X_3-gas is perhaps HH_2, since copper yields two types of hydrides, and the uniformity of the table is improved thereby. That is to say, such a compound would find a place in the table and give it a more symmetrical appearance. Thomson gives reasons based upon experiments for *not* expecting hydrogen to form a compound " H_3." Still the point is not settled (see *Nature* xc., 645).

Radium being closely allied to barium, and actinium to lanthanum, perhaps justifies, in a measure, the assumptions that these elements are capable of forming hydrides as shown.

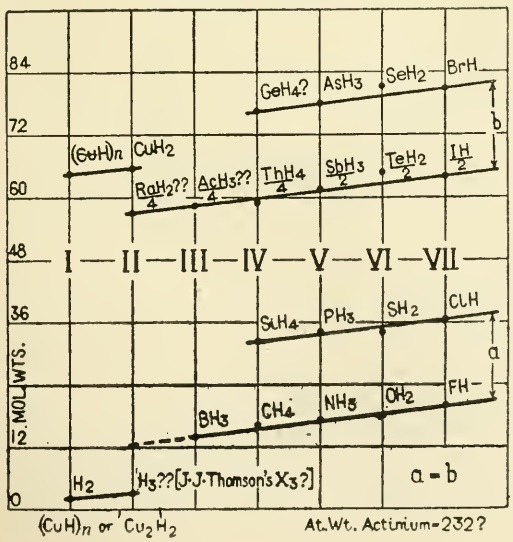
TABLE I.*

Group No.			Group No.
I.	HH	LiH, NaH, KH, RbH, CsH	I.
II.	$[HH_2??]$	CaH_2, SrH_2, BaH_2	II.
III.	BH_3	LaH_3, CeH_3	III.
IV.	CH_4, SiH_4	ZrH_2?	IV.
V.	NH_3, PH_3	(NbH)	V.
VI.	OH_2, SH_2		VI.
VII.	FH , ClH		VII.

Group No.			Group No.
I.	$(CuH)_n$		I.
II.	$[CuH_2]$, RaH_2??		II.
III.	AcH_3??		III.
IV.	GeH_4 ?, ThH_4		IV.
V.	AsH_3 , SbH_3		V.
VI.	SeH_2 , TeH_2		VI.
VII.	BrH , IH		VII.

* This table is similar to one appearing in a small book by the author, entitled " Studies in Valency," now in press.

TABLE II. (Diagram).



The straight lines in the diagrammatic table bring into prominence a fact observed before, that the irregularity in the atomic weight of tellurium is shared to some extent by selenium, since it is not supposed that the atomic weights are sufficiently in error to expect the values to fall exactly on a straight line. The method therefore not being exact, one is led to expect the atomic weight of actinium to be in the *neighbourhood* of 230.

Of course some of the hydrides shown in these tables are extremely unstable, and their formulæ are not all confirmed by vapour density determinations.

It may be that a classification based upon the atomic values *within* a bracket—$(MH_n)_{n'}$—are the ones which will lend themselves to a more systematic treatment (see copper in Table II.). [M = element other than hydrogen ; H = hydrogen ; n and n' = numbers 1, 2, 3, &c.].

Royal Institution.—On Tuesday next, April 29th, at 3 o'clock, Prof. William Stirling begins a course of three lectures at the Royal Institution on " Recent Physiological Inquiries." Owing to the illness of Prof. Bateson, his course of lectures on " The Heredity of Sex and some Cognate Problems " has been postponed. In addition to those Friday Evening arrangements already announced, Discourses will probably be given by Mr. F. Balfour Browne, Capt. C. G. Rawling, Prof. Silvanus P. Thompson, Mr. Owen Seaman, and Dr. Francis Ward.

THE TESTING OF SAFETY EXPLOSIVES.*

By Prof. VIVIAN B. LEWES, F.I.C., F.C.S., &c.

(Continued from p. 190).

In making the dust-and-air mixture, its sensitiveness will depend upon (1) the ease of ignition of the dust, the degree of fineness to which it is reduced, and the other factors which have been studied so fully at Altofts and Eskmeals, one of the most important being its freshness; (2) the percentage of dust to air at the moment the shot is fired into it; and (3) the percentage of oxygen in the air.

Through the courtesy of Major Cooper-Key, I obtained a sample of the dust used at Rotherham, which is made by grinding coal from the 7-ft. seam of the Birchenwood Colliery, North Staffordshire, to a powder that will pass a 150-mesh sieve. On analysis, the dust gave:—

Moisture	2·40
Volatile matter	29·60
Fixed carbon	65·41
Ash	3·94

whilst its ignition point was 400° C.

It is evident, therefore, that if the coal-dust be suspended in pure air with a percentage of 20·9 of oxygen, as soon as the temperature is raised for a sufficient length of time to 400° C. the dust will ignite.

In the second report of the Explosions in Mines Committee, the "relative ignition temperatures" of a long series of coal-dusts, as determined at Eskmeals, are given, and out of fifty dusts two only are credited with an ignition temperature below 1000° C. (*i.e.*, 950° C.), and four are above 1400° C.

Amongst these the sample N 216 has much the same proximate composition as the Rotherham dust, and is credited with a "relative" ignition temperature of 1065° C.

An examination of the method employed shows that what has been determined is the relative ease of ignition under certain circumstances, and has nothing to do with the ignition point. Coal dust has been blown at a definite pressure through a glass tube, across which a spiral of platinum wire, coiled on a quartz tube, was arranged and heated to measured temperatures, and the degree at which the rapidly passing cloud caught fire was the "relative" ignition temperature.

The Eskmeals experiments are of great interest from another point of view. We saw that the French Commission found that methane, or, rather, pit-gas, inflamed at a temperature of 650° C. continued for ten seconds, but needed a much higher temperature to give immediate ignition, and it appears probable that coal-dust, although ignited by a heat of 400° C. continued for a few seconds, requires a temperature of over 1000° C. for immediate ignition; but further experiments are needed to establish this point, as extended experience will probably show that the gases occluded in the coal dust, especially oxygen, play an important part in the temperature at which ignition takes place, and the dusts tested at Eskmeals were all dried at 107° C. for an hour before being experimented with, which would expel gases or, in any case, alter their nature.

These points, however interesting from a theoretical point of view, have but little to do with the subject we are discussing, and the fact remains that the dust used at Rotherham is sensitive, is all obtained from one seam in the same colliery, and is either freshly ground for each testing, or is kept from contact with air in sealed tins, so that every requirement is satisfied.

We next come to the influence of the percentage of dust in the test mixture.

M. Watteyne has made experiments on this point at Frameries, and has found that it has a very marked influence on the *charge limite* of explosives. In one case, with 38 per cent dust, the explosive fired the mixture with 200 grms., whilst it took over 600 grms. to fire it when there was only 10 per cent of dust; with another explosive the 38 per cent mixture was fired with 400 grms., and when the dust was reduced to 15 per cent it was not fired with over 700 grms.

At both Rotherham and Frameries the percentage of weight of dust to air in the gallery is approximately 10, but as the dust is raised by the explosive wave, the percentage present in the path of the outrush of heated products is probably far higher, and will vary probably with the kind of explosion. It is felt, however, that having the dust at rest resembles more nearly the conditions existing in a mine, where it is mostly raised by the explosion itself.

Great care is taken to allow time for the products of combustion from one shot to clear from the gallery before another test is made, as any products of combustion left would, by reducing the percentage of oxygen in the air, render the next test less sensitive.

At every testing station it has been recognised that the apparatus had its good and bad days, and that there were undoubtedly meteorological conditions which affected seriously the results of the testings, but what the interfering factors were has never been satisfactorily explained.

Early this year some experimental shots were fired at Rotherham with two explosives which proved thoroughly satisfactory, one failing to ignite gas or dust with a 32-oz. charge, the other proving safe with 30 ozs., and as they were both stronger than most explosives that showed any promise of passing, the manufacturer was naturally elated, but decided wisely to have some more experimental shots fired with cartridges from the same batch before sending in the explosives for the official test. Both mornings were raw and cold, the explosives were the same batch, the dust freshly ground in each case, and the tests carried out under identical conditions, yet both explosives gave fierce ignition with small charges in dust, although the results in the gas mixture were the same as before.

The only difference between the two sets of experiments was that the first, when the explosives would have passed with the highest maximum charge, were carried out when there was an abnormally low pressure, the barometer standing at 29·3 ins., whilst the second set, in which both failed, were made with the barometer standing at 30·2.

The difference of an inch in the barometric column makes a difference of about 3 per cent in the weight of the oxygen present in a cubic foot of air, and this is probably the factor that made the difference between passing the test with a 32-oz. maximum charge and firing the coal-dust mixture with a small charge. I know that some authorities consider it is the volume and not the weight of oxygen in air that counts, but it seems to me that it must be the number of molecular contacts in a combining mixture that governs the rate and ease of combination; and if experience proves that pressure has this effect, what becomes of our tested safety when the explosives are used at the pressures existing in a deep mine? At any rate, if I may make the suggestion, it seems worth while to take advantage of all abnormal variations in pressure to see if any difference is noticeable in the sensitiveness of the coal-dust mixture when well-standardised explosives are fired into it, and, if this result is proved, to fix a barometric limit for days on which testings shall be made for the permitted list.

So far my criticisms—whatever they may be worth—have been directed to the conditions of the new tests, and now I want to call your attention to the nature and characteristics of the explosives that will be devised to enable them to pass for the permitted list.

The apparatus at Woolwich was altogether too small to obtain any definite information as to the alteration in "maximum charge" likely to be brought about by doing away with tamping; but some experiments have been made upon this point at Frameries which go to show that the wetter dynamites suffer the least, having the *charge limite* reduced only by one-half, whilst explosives con-

* A Paper read before the Royal Society of Arts, April 2, 1913.

taining mixtures of nitrated aromatic hydrocarbons and oxidising compounds suffer most, and have their *charge limite* reduced to one-tenth of what it would be with even a 4-in. tamping.

It is clear, therefore, that most of the explosives on the old permitted list will fail to pass the new tests with a "maximum charge" of even 8 ozs., whilst the Rotherham conditions of test are so sensitive that many of the S.G.P. explosives on the Belgian list will also fail.

There are two definite compounds known which can be exploded by detonation, and yield sufficient oxygen to complete the combustion of the inflammable part of their structure, and these are nitroglycerin and ammonium nitrate, both of which yield nothing but gaseous products which contain an excess of oxygen.

The nitroglycerin is one of the most powerful and hottest explosives known; the ammonium nitrate is a feeble explosive difficult to detonate completely and cool in explosion.

(To be continued).

THE LATEST ACHIEVEMENTS AND PROBLEMS OF THE CHEMICAL INDUSTRY.*

By CARL DUISBERG.

Probably in no domain of human knowledge and endeavour have the combined forces of theory and practice, intimately acting and reacting upon each other, made such immense strides and led to the solution of such difficult problems as in the Chemical Industry, an industry which, indeed, had its beginnings in the distant past, but in its vast development and international character is essentially a child of modern times. Success has so emboldened this industry that it considers itself capable of solving any problem, provided the men in its service are well trained in theory and practice, and ready to devote themselves to the best of their ability, with patience and perseverance, to the object in view. This has been shown by the struggle between the contact process of producing sulphuric acid and the old "chamber process," by the rivalry between the Solvay process and the Le Blanc method in the manufacture of soda; by the production of nitric acid and its salts by direct oxidation of nitrogen of the air under the influence of the heat of the electric discharge; by the manufacture of ammonia from atmospheric nitrogen indirectly *via* calcium cyanamide, and directly by combination with hydrogen; by the replacement of madder by alizarin, and of natural by synthetic indigo, as well as by innumerable other instances in the colour, perfume, and pharmaceutical industries.

If I venture before an audience not wholly consisting of chemists, within the brief period of an hour, to describe the latest achievements of the chemical industry and to recount the problems that are engaging our attention, I must restrict myself to a great extent both in the choice of the subject matter and its mode of presentation. We can, indeed, merely touch upon the most important happenings in our industry, and must from the very outset refrain from a thorough discussion of the subject, either from the purely chemical or the technical side. However, what cannot be described for lack of time, and what we should very much like to add for the sake of those chemists who are present, is illustrated by our rich collection of diagrams, products, and materials of all kinds. What can neither be mentioned in my paper nor illustrated by these exhibits will be demonstrated by means of lantern slides, and, should you possess patience enough, I shall show you at the conclusion of my address one of the newest factories which the German Chemical Industry has built on the Rhine, with its various manufacturing departments, and, above all, its provisions for the welfare of its employees.

In the spirit of Faust, "Who brings much will bring something to many," I invite you to make a flight with me in an airship, as it were, over the fields where the Chemical Industry holds sway, and, from our point of vantage, to take a bird's-eye view of the latest achievements of this industry. Now and then, we shall make a landing and examine the most attractive features a little more closely.

Production of Power.

The question of power, which is of the utmost importance in every industry, and especially in the great synthetic processes by means of which nitric acid and ammonia are manufactured, is now dominated by the perfected utilisation of hydraulic power and the development of the turbine. Not only does the transmission of electric energy render it possible to utilise water power at great distances, but it also permits the transmission of power evolved at the coal mines and the peat fields to distant points, thus eliminating the necessity of transporting the fuel itself. Recently, we also learned to apply the principles of the water turbine to the steam turbine. But this advance over the piston steam engine, which Watt so ingeniously constructed about 150 years ago, has already been surpassed by benzene, petroleum, or oil motors (Diesel motors), and, above all, by the reliable gas engines which are driven by blast furnace gases, Mond gas, and, more recently, by peat gas.

Production of By-products.

The manufacture of by-products goes hand-in-hand with this more direct generation of energy from fuel. These products include ammonium sulphate, of such great importance in agriculture, and the tar distillation products so indispensable in the colour industry. The latest and most rational method of utilising the peat or turf beds, so plentiful in Germany and in many other countries, is practised in Schweger Moor near Osnabrück according to a process discovered by Frank and Caro. There peat gas is produced and utilised and ammonia obtained as a by-product, the required power being generated in a 3000 h.p. central electric power station. The moorland, after removal of the peat, is rendered serviceable for agricultural purposes.

At that place nearly 2500—2600 cubic metres of gas with 1000—1300 calories of heat were obtained from 1000 kg. of absolutely water-free peat in the form of air-dried peat with 45 to 60 or 70 per cent of moisture. This gas represents energy equal to 1000 h.p. hours, equal to 700 kilowatt hours, after deducting the heat and power used for the operation of the gas works. In addition 35 kg. of ammonium sulphate were produced from the above quantity of peat which contains 1 per cent of nitrogen.

The greatest problem of power production, the direct conversion of coal into electric energy by means of gas batteries, a problem which we had hoped to solve twenty-five years ago, is still to-day nothing more than a dream.

Production of Cold.

Besides the problem of power and heat, the question of refrigeration is one of growing importance to the chemical industry. Instead of the ammonia machines with which a temperature of -20° C. can be attained, we employ to-day sulphurous acid machines, or, better still, resort to the carbonic acid gasifier, which yields a temperature of -40° C. It is hoped in the near future to produce refrigerating machines which, by the use of suitable hydrocarbons, will give temperatures of -80° C. Plants for the liquefaction of air, producing as low a temperature as -190° C., are becoming more and more common, and are especially profitable where gas mixtures, rich in oxygen, or where pure nitrogen, which is simultaneously produced, can be utilised. Diagrams showing the process invented

* General lecture by Geheimer Regierungsrat Prof. Dr. Carl Duisberg, Managing Director of the Farbenfabriken of Elberfeld Co. Eighth International Congress of Applied Chemistry, New York.—From the *Journal of Industrial and Engineering Chemistry*, iv., No. 10.

by Linde for the rectification of liquid air with the object of isolating nitrogen and oxygen are exhibited here. The Badische Anilin und Soda Fabrik in Ludwigshafen on the Rhine intends to manufacture hydrogen from water-gas in a similar way, and to utilise the carbon monoxide, which is simultaneously obtained, as a source of power. In a large plant which is being erected, the firm is going to produce ammonia synthetically by combining, according to Haber's invention, pure nitrogen, obtained by the liquefaction and rectification of air, with hydrogen manufactured as above. Particulars about this process will be given during the Congress by Prof. Bernthsen in his lecture on "Synthetic Ammonia."

Size of Apparatus.

Influenced by the Solvay process for the manufacture of soda and its pecuniary advantages, the apparatus used in the chemical industry have enormously increased in size. In this respect the United States, no doubt on account of the example set by the iron industry with its blast furnaces with a daily capacity of 500 tons, its giant conveyers (50-ton waggons), its huge hoisting cranes, is ahead of other countries. But careful calculations have proved that there is a limit in this direction. The failure, on account of size, of the Mactear sulphate furnace, with a daily output of 25 tons, is well known, while the mechanical sulphate furnace of the Verein Chemischer Fabriken in Mannheim, which produces only 7 tons a day, is a success everywhere. It is not improbable that the high cost of construction and the great loss which accidental stoppage entails will necessitate a reduction in size of the wonderful Wedge furnace, a creation of the United States, which roasts 30 tons of iron pyrites per day.

In the organic chemical industry, the iron vessels for chlorination, sulphonation, nitration, reduction, and oxidation, as well as the wooden tanks in which we diazotise and produce colours, have developed from the small vessels and vats of former years into apparatus of mighty size, their limit being generally determined by the capacity of the mechanical industry. But here, too, the mistakes which often occur in manufacturing processes and the extra losses which they involve teach us that a wise moderation should be exercised.

Wherever possible, continuous operations have replaced those processes which worked intermittently. In this way loss of time and expense, caused by cooling and re-heating, are avoided. This is exemplified by Uebel's new method of the production of nitric acid from Chili saltpetre with retorts lying above each other and without stirrer, and by that of the Badische Anilin und Soda Fabrik, where the chambers are back of each other, with stirrer, these methods having replaced the old single retort process.

(To be continued).

GERMAN CHEMICAL WORKS.

According to a writer in the *Revue Générale de Chimie*, the success of the German Chemical Works is not due so much to the value of the chemists, cheap labour, and legislation as it is to the marvellous systems of organisation. The following are some of the interesting points brought out in the French paper.

The managers of works are usually young, men of an age when the faculties are fully developed. The writer expressed his astonishment at hearing that a manager of forty-five years had been pensioned off. "Why not?" was the reply he received. "He has been ten years with the firm, and during that time must have practically applied all his ideas. There would be the risk of his being influenced later by routine and opposing the opinions of younger men. We must make use of the energy of others capable of valuable initiative."

The sites of new works are chosen solely from the point of view of facilities for transport and convenience in arrangements. Little attention is given to anything else. If workmen live a long way off they are brought to the works by boat or rail. If there are no towns about, one is built near the works for the express purpose of attracting labour. . . . The number of workmen is very small compared with the dimensions of the works in which they are employed and the number of machines in use. Mechanical perfection is such that labour is reduced to a mimimum, a large number of duties being limited to mere supervision. . . . Thus, in a refrigerating plant a single workman, seated in a hut, sets all the plant working.

There are technical libraries of great value in the works, containing periodicals, books, patent specifications, scientific papers, and everything relating to industrial chemistry. Specialists are constantly engaged in reading and making notes under the instructions of the research experts.

Catalogues are printed in the works' own printing offices. These volumes are presented to all clients, and also to scientists and technical journals interested in the subjects. The extraordinary regularity in the development of each group of works is remarkable. At the famous "Badische" of "Bayer" the number of workmen has been about doubled every five years since the foundation. Immediately one particular line of manufacture is played out other productions are taken in hand. In new works there are, consequently, empty spaces near most of the machines, where others can be mounted when consumption attains a certain degree. Likewise, spaces are left between the buildings to erect other structures.—*Chemical Engineer*, xvi., No. 5.

THE SCIENTIFIC WEEK.

A Gigantic Electro-magnet.

The most powerful electro-magnet of the world will soon be installed in the laboratories of Prof. Becquerel at the Polytechnic School of Paris.

This electro-magnet, constructed by Prof. Pierre Weiss, of the Polytechnicum of Zurich, will have a minimum electromagnetic force of 50,000 gauss.

At the present moment three electro-magnets attain 45,000 gauss. They are the electro-magnet of the Polytechnicum of Zurich, Prof. Kayser's one at the University of Bonn, and the one belonging to Prof. Ams, in the United States.

It is the utilisation of *ferro-cobalt* for the constitution of the polar pieces that will allow this force of 50,000 gauss to be attained. A new system of cooling with water will allow the electro-magnet of Jean Becquerel to work without interruption for twenty-four hours at a maximum force, whilst existing apparatuses can rarely work for more than one or two hours.

The dimension of the polar pieces is 16 centimetres and a-half. The distance between the two poles can attain 2 millimetres at the most. It is in this little space that the molecules of the bodies which the physician may wish to examine will be submitted to the torture of the magnetic effects.

The electro-magnet will work under a power of 200 to 250 ampères and 110 volts.

The first experiments that Jean Becquerel will attempt will aim at elucidating the obscure points of Zeeman's phenomenon.

"We know, says he, that there is something unknown in this phenomenon, something that is at the limit of visibility with our present instruments. I hope that with my new electro magnet I shall be able by the help of a few extra gauss, to render visible that phenomenon which explains the secret structure of matter. Molecular and atomic life will perhaps deliver up to us a part of its secret.

When once these experiments are finished I shall continue by the study of magnetic effects on matter."

Physicians, however, hope that an international understanding will facilitate the construction—in a not too distant future—of an electro-magnet of a formidable power, able to attain the million of gauss. This wish was expressed by the last international congress of electricians.

According to Ch. Ed. Guillaume, assistant-director of the International Bureau of Weights and Measures, the total cost of this giant electro-magnet would attain the price of a modern dreadnought, that is to say, from 60 to 70 millions of francs.

Mesothorium is Three Hundred Times more Active than Radium.

Dr. Ledoux-Lebard has just studied the effects of the radio-active substances of the thorium series, and especially of a body discovered by the German chemist Hahn called *mesothorium*, and which is in many ways a succedaneum of radium. The mesothorium would possess, however, at an equal weight, an activity about 300 times greater. This body, which is extracted from the monazite sands of Brazil and from the residuum from the fabrication of the "Auer" gas mantles, costs half the price of radium. Its use is then even now interesting whenever the product is to be lost (injections, draughts).

The observations of the author have shown him that with malignant tumours, especially ulcerated cancers of the breast, a notable diminution of pain is often obtained by injections of mesothorium. This method seems to raise the general state of unoperable cancer patients.

A New War-Bread.—Oatmeal Soup.

Soldiers are going to receive a new war-bread, made after a recipe kept secret by the technical section of the commissariat, and which has just been experimented with success by the troops in the East.

This product is in the form of little small biscuits, and contains a certain quantity of sugar and purified vegetable fat which gives it an agreeable taste, while furnishing to the muscles of the consumers a supplement of carbon which allows them to accomplish a stronger effort.

The men consumed two biscuits in the morning coffee, one in the soup, eight as table bread.

The taste of this war-bread, which recalls a little that of the *petit beurre biscuits* or of the Japanese *katapan*—sweet biscuits that are distributed to the troops in the field—is more agreeable than the former one; its aspect is also more appetising, and it was eaten with satisfaction, especially with the coffee and as table bread.

Its prolonged use caused no gastro-intestinal indisposition, neither did it provoke, as its predecessor, the disagreeable "biscuit diarrhœa."

The utilisation of oats has also been tried in a very interesting way as an aliment for the soldier in the field. During thirty consecutive days a company of infantry received a soup of torrefied oatmeal. During the first fifteen days this company marched 340 kilometres. During the other fifteen days it accomplished manœuvres in camp.

Now, during these thirty days no man of this company went on the sick-list, whilst in each of the three other companies of the same battalion which accomplished the same marches and the same manœuvres, eight or ten men went every day to the doctor's consultation.

The Sun is the Coldest of the Stars.

Dr. Rosenberg, astronomer at the Göttingen Observatory, has just published the very interesting results that he has obtained relating to the temperature of the stars, by means of a very ingenious photographic method. It is known that when the temperature of an incandescent body is raised, as, for example, when a piece of metal is gradually heated or when a current gradually more and more intense is passed into a metallic filament, not only the quantity of light emitted by the body is augmented, but the composition of this light varies and it becomes more and more rich in blue rays and poorer in red rays. That is why piece of iron heated progressively becomes first dark red, then sherry-red, then orange, then dazzling white. Now, the proportion of red rays to the blue ones, or more generally that of any colour to another colour, is bound to the temperature of the incandescent body by a very simple law that has been verified in large limits, and, moreover, established theoretically by the German professor Planck.

Dr. Rosenberg has then photographically determined the relative intensity of rays of different colours in the spectrum of about sixty stars, and he deduces from it, by the law of Planck, their temperature. It is thus that he finds for the temperature of the sun 4950°, for Aldebaran (the beautiful star in the Taurus constellation) 2150°, for Arcturus 3100°, for the Polar star 5200°, for other stars still much higher temperatures:—Alpha, Eagle, 10,500°, Véga 22,500°, Sirius 27,500°; at last Rosenberg has found about ten stars the temperature of which exceeds 40,000°. Already M. Nordmann, of the Paris Observatory, had announced that the temperature of certain stars exceeds 40,000°, and if we compare the results that he had obtained a few years ago by means of his pyrometer *stellaire* with those that Rosenberg has just published, we find a remarkable concordance between the relative results of the same stars, although two astronomers have employed very different methods and have not studied the same rays of the stars, since Nordmann operated on visible rays and Rosenberg on photographic rays. We may then now consider the study of the temperature of the stars as having entered a definite way. This study has already proved that the sun is undoubtedly one of the coldest of the stars, and this shows us how low are the temperatures realisable on the earth compared to those realised in the heavens, since the hottest object that we can obtain, the positive crater of the electric arc, is only about 3500°, that is to say, a temperature still far below that of the sun itself and of most of the stars.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, April 10th, 1913.

Sir Alfred Kempe, Vice-President and Treasurer, in the Chair.

Papers were read as follows:—

"*Effect of Lability (Resilience) of the Arterial Wall on the Blood Pressure and Pulse Curve.*" By L. Hill, F.R.S., and M. Flack.

"*Nature of the Toxic Action of the Electric Discharge upon* Bacillus coli communis." By Prof. J. H. Priestley and R. C. Knight.

1. Electric discharge in air is fatal to bacteria exposed to its action.

2. The effect is due to the products of the interaction of the constituents of the air, namely, nitric acid and nitrous acid and ozone.

3. Discharge in air-free hydrogen has no deleterious effect on the organisms, but the presence of small quantities of air allows the formation of a toxic substance, probably hydrogen peroxide, which again exerts a bactericidal action.

4. It therefore follows that electric discharges in which the current density does not exceed 10-5 ampères per square centimetre do not exert any directly toxic action upon micro-organisms, a result which is contrary to the statements made by some previous investigators.

"*Some Investigations on the Phenomena of 'Clot' Formation.* Part I. *On the Clotting of Milk.*" By S. B. Schryver.

"*Morphology of Various Strains of the Trypanosome causing Disease in Man in Nyasaland.* II. *The Wild Game Strain.*" By Surg.-General Sir D. BRUCE, F.R.S., Majors D. HARVEY and A. E. HAMMERTON, and Lady BRUCE.

"*Morphology of Various Strains of the Trypanosome causing Disease in Man in Nyasaland.* III. *The Wild* Glossina morsitans *Strain.*" By Surg.-General Sir D. BRUCE, F.R.S., Majors D. HARVEY and A. E. HAMERTON, and Lady BRUCE.

"*Infectivity of* Glossina morsitans *in Nyasaland.*" By Surg.-General Sir D. BRUCE, F.R.S., Majors D. HARVEY and A. E. HAMERTON, and Lady BRUCE.

CHEMICAL SOCIETY.

Annual General Meeting, March 14th, 1913.

Prof. PERCY F. FRANKLAND, LL.D., F.R.S., President, in the Chair.

MR. C. H. HAMPSHIRE and Mr. T. R. Merton were appointed Scrutators, and the ballot was opened for the election of Officers and Council for the ensuing year.

The PRESIDENT presented the Report of the Council on the progress of the Society from January, 1912, to date, and a statement was made by the TREASURER as to the Income and Expenditure for 1912. The adoption of the Report of the Council, together with the Balance Sheet and Statement of Accounts for the year ended December 31, 1912, was proposed by Mr. T. FAIRLEY, seconded by Prof. A. G. GREEN, and carried unanimously.

A Vote of Thanks to the Auditors was proposed by the TREASURER, seconded by Dr. S. B. SCHRYVER, and acknowledged by Prof. J. M. THOMSON.

Report of Council, 1912—1913.

The Annual Reports of the Council have, in the past, dealt with the work of the Society during the previous calendar year, but the general portion of the present Report refers to the period from the commencement of 1912 to March, 1913, and this portion of future Reports will concern the period from one Annual General Meeting to the next Annual General Meeting.

On December 31, 1911, the number of Fellows was 3104. During 1912, 184 Fellows were elected, and 7 have been reinstated, the gross total being 3295. The Society has lost 33 Fellows by death, 52 have resigned, 1 has been elected an Honorary and Foreign Member, the elections of 4 Fellows have become void, and 47 Fellows have been removed for non-payment of Annual Subscriptions.

The total number of Fellows therefore on December 31, 1912, was 3158, showing a net increase of 54 over the preceding year. The number of Fellows elected during 1912 exceeds the average for the past six years by 21 Fellows, and the small net increase in the number of Fellows is accounted for by the large number of resignations and of Fellows removed for non-payment of Annual Subscriptions.

The names of the deceased Fellows, with the dates of their election, are :—G. Attwood (1872); A. E. Beanes (1902); A. H. Black (1879); R. H. M. Bosanquet (1865); J. M. Cameron (1875); M. Coupe (1905); E. Divers (1860); A. E. Elkins (1883); A. J. Elkington (1911); J. O. Ferrier (1902); A. Fraser (1867); T. Griffiths (1879); A. Hill (1882); R. Howell (1880); O. C. Johnson (1897); H. O. Jones (1900); D. S. Kemp (1867); W. F. Laycock (1890); T. D. Lichtenstein (1878); C. W. Low (1884); J. McArthur (1887); W. Masters (1873); H. de Mosenthal (1890); B. E. R. Newlands (1864); J. Pattinson (1863); B. V. Rao (1911); A. Richardson (1883); H. Salt (1863); H. Seward (1870); W. R. R. Starling (1906); J. P. Strangman (1887); J. Wade (1890); W. O. Wootton (1908).

At the end of 1911 the number of Honorary and Foreign Members was 31. Since that date the Society has mourned the loss of Lecoq de Boisbaudran and J. W. Mallet, whilst on March 7, 1912, P. A. Guye, T. B. Osborne, P. Walden, and R. Willstätter were elected. The total number of Honorary and Foreign Members therefore at the present time is 33.

The Council has great pleasure in offering hearty congratulations to the following, who, in 1912, attained their Jubilee as Fellows :—William Esson, elected May 1, 1862; William Adam Dixon, elected December 18, 1862; Edmund James Mills, elected December 18, 1862.

The Council desires to record its high appreciation of the services rendered to the Society over a period of eight years by the retiring Senior Secretary, Prof. Crossley. Prof. Crossley's tenure of this arduous office has been distinguished by great administrative skill, by sound judgment, and by unfailing tact. The Society is deeply indebted to him for the generous manner in which he has placed his time and energies at its disposal.

During the year, 336 scientific communications were made to the Society, 256 of which have been published already in the *Transactions*, and abstracts of all have appeared in the *Proceedings*.

The volume of *Transactions* for 1912 contains 2568 pages, of which 2431 are occupied by 266 memoirs, the remaining 137 pages being devoted to the Obituary Notices, the Becquerel, Cannizzaro, and Moissan Memorial Lectures, the Report of the International Committee on Atomic Weights, the Report of the Annual General Meeting, and the Presidential Address; the volume for the preceding year contains 259 memoirs which occupy 2270 pages.

The *Journal* for 1912 contains 5497 abstracts, which extend to 2264 pages, whilst the abstracts for 1911 numbered 5236, and occupied 2200 pages. The abstracts may be classified as follows :—

	Pages.	No. of Abstracts.
PART I.		
Organic Chemistry	1044	1796
PART II.		
General and Physical Chemistry ..		1238
Inorganic Chemistry..		493
Mineralogical Chemistry		120
Physiological Chemistry		737
Chemistry of Vegetable Physiology and Agriculture		385
Analytical Chemistry		728
	1220	3701
Total in Parts I. and II. ..	2264	5497

The possibility of Fellows resident abroad procuring through the Society fuller abstracts of papers than appear in the *Journal* has been under consideration, and the Council has decided :—

"That persons requiring expanded abstracts or translations of papers published in other journals should apply to the Editor. Ten shillings per printed page (about 500 words) will be charged, and payment should be made to the Editor at the time the request for a translation or fuller abstract is forwarded to him."

The Council has also resolved :—

"That in order to obtain a more equal division of abstracts, those of Physiological Chemistry and the Chemistry of Vegetable Physiology and Agriculture shall, in future, be included in Part I. of the Abstracts, instead of in Part II."

Volume V. of the Collective Index of the *Journal* and *Proceedings* of the Chemical Society (1903—1912) will be issued in two parts: Part I. (Author Index) in 1913, and Part II. (Subject Index) in 1914. Such prompt publication of the Collective Index is rendered possible by the system employed for the preparation of the Annual Indexes,

as the work done in connection with the latter can be largely utilised for the Collective Index.

The *Transactions* for 1912 contain Obituary Notices of Walthère Spring and Louis Joseph Troost, Honorary and Foreign Members. Obituary Notices also appear of John Attfield, John Muter, and Nevil Story-Maskelyne, and the Council expresses its thanks to those gentlemen who have kindly prepared these notices.

The Society was represented at the funeral of the late Lord Lister by the President.

Since the last Report was published, the Society has had the privilege of listening to an account of the life and work of—(*a*) S. Cannizzaro, from Sir William Tilden; (*b*) H. Moissan, from Sir William Ramsay; (*c*) H. Becquerel, from Sir Oliver Lodge.

The Council has considered the desirability of issuing a second volume of Memorial Lectures, and has decided to postpone the publication until after the delivery of the Ladenburg Lecture by Prof. Kipping and the van't Hoff Lecture by Prof. James Walker, both of which lectures, it is hoped, will be delivered before the close of the present Session.

The President, Prof. P. F. Frankland, was the official representative of the Society at the celebration, in July, 1912, of the 250th Anniversary of the Foundation of the Royal Society, when an Address of congratulation was presented on behalf of the Chemical Society. The text of the Address appeared in the *Proceedings* (vol. xxviii., p. 248).

The Eighth International Congress of Applied Chemistry held in Washington and New York in September, 1912, was attended by Dr. M. O. Forster, Sir William Ramsay, and Sir Boverton Redwood as delegates of the Chemical Society.

The Society was represented at the Centenary Anniversary of the Academy of Natural Sciences of Philadelphia in March, 1912, by the late Prof. J. W. Mallet and by Prof. Alexander Smith; at the Bicentenary Festival of the Medical School, Trinity College, Dublin, in July, 1912, by Prof. G. T. Morgan; and at the 25th Anniversary Celebration of the Verein Deutscher Chemiker by Dr. R. Messel.

During the Summer Vacation of 1912 the Society's rooms were redecorated throughout. After consultation with the architect originally responsible for the scheme of ventilation in the Meeting Room, the Council also decided to place a large suction-fan in the roof over the Library, directly connected with the ventilating flues of the Meeting Room. This has had the result of materially improving the atmosphere of the room.

A conference of representatives of those Chemical Societies in Great Britain publishing abstracts of papers appearing in other journals is taking place, at the suggestion of the Council, to consider the possibility of decreasing the cost of production of such abstracts. Delegates have been appointed by the various Societies as follows:—

Society of Chemical Industry—R. Messel, J. Lewkowitsch.

Society of Public Analysts—L. Archhutt, H. D. Richmond, O. Hehner.

Institute of Brewing—J. L. Baker, A. R. Ling.

Institute of Metals—W. Rosenhain, G. S. Scott.

Society of Dyers and Colourists—E. Knecht, W. M. Gardner.

Iron and Steel Institute—J. E. Stead, G. C. Lloyd.

The Council Meetings of the International Association of Chemical Societies held in Berlin in April, 1912, were attended by the three representatives of the Society, Prof. A. W. Crossley, Prof. P. F. Frankland, and Sir William Ramsay, and an account of the work of the Council appeared in the *Proceedings* for 1912 (p. 201). The General Expenses of the Association for the previous year amounted to £60, of which sum the share of the Chemical Society was £10 6s. 7d.

The next meetings of the Council will be held in London during September, 1913, and the Officers of the Association are—Sir William Ramsay (President), Prof. Percy F. Frankland (Vice-President), Prof. Arthur W. Crossley (General Secretary), who remain in office until the end of the meeting.

The Society has received through Sir Edward Thorpe the Annual Report of the International Committee on Atomic Weights, 1913, together with a Table of Atomic Weights. The Report appears in the *Proceedings*, p. 213, and in the *Transactions*, p. 1829.

The Council has made a further donation of £10 to the International Commission of Publication of Annual Tables of Constants and Numerical Data, Chemical, Physical, and Technological.

In the last Report it was mentioned that it was proposed to raise a Memorial to the late Prof. J. H. van't Hoff, and that subscriptions would be received by the Treasurer. The sum of £65 4s. was subscribed by Fellows and forwarded to the Memorial Committee.

The Council has considered a request from the Director of the Municipal Laboratory of Paris for permission to arrange for the preparation of a French translation of the Annual Reports, and has agreed to the proposition. The publication of the work will be carried out by Messrs. Hermann et Fils, of Paris.

At the request of the Rev. W. G. Searle, Keeper of Coins at the Fitzwilliam Museum, Cambridge, the Council has presented to the Museum copies of the Longstaff Medal and Faraday Medal.

The number of books borrowed from the Library during the year was 1825, as against 1808 during the previous year; of these 491 were issued by post, as against 419 in the preceding year.

The additions to the Library comprise: 135 books, of which 70 were presented; 482 volumes of periodicals (representing 237 journals), and 76 pamphlets; as against 171 books, 438 volumes of periodicals (representing 237 journals), and 87 pamphlets last year.

The Library is indebted to Mr. J. A. Audley for a welcome gift of early journals.

The yearly increasing size of the Library will necessitate the consideration in the immediate future of the provision of adequate accommodation for its growth. In a statement of the Librarian appended to the President's Address in 1890, it was recorded that the Library then contained 9884 volumes, made up of 3082 volumes of systematic works, and 6802 periodicals, with the addition of 1450 pamphlets. At the present time it is estimated that the Library contains 21,256 volumes, of which 5983 are systematic works, 15,273 volumes of periodicals, together with 3500 pamphlets. It is thus seen that in twenty-two years the periodicals in the Library have increased in number of volumes by 124·5 per cent, the systematic works by 94 per cent, and the general total by 115 per cent.

It is estimated that shelf-room for 7000 volumes will be required to accommodate the increase of volumes for the next ten years. At the close of 1913 there will at least be an additional 650 volumes to accommodate, whilst the empty shelving now at liberty will only contain some 250 volumes. Therefore, not only in the future, but also for the immediate present, additional Library accommodation is essential, and the Council has referred this question to the House and Library Committees.

Taking into account the occurrence of some items of exceptional expenditure, such as the decoration of the whole building and the ventilation of some of our rooms, it is satisfactory to find that, after meeting these expenses out of the income for the year, there is still an excess of income over expenditure of £176 1s. 7d. In 1913 the needs of the Library in the direction of providing accommodation for its continuous growth will necessarily entail considerable outlay, as pointed out above. For 1912 the income from all sources amounted to £8120 12s. 3d., and the expenditure to £7944 10s. 8d.; for 1911 the corresponding amounts were £7735 11s. 6d. and £7499 3s. 10d. respectively. In other words, our income has increased by £385 0s. 9d., and our expenditure by £444 16s. 10d. The redecoration, improvements in ventilation, &c., alone

account for £265 of this, and the increase in cost of the *Journal* for £124 2s. 8d.

As it was found impossible without either realising some of our investments or raising the annual subscription to give to Fellows without charge Vol. V. of the Collective Index, the price charged for it (30s.) was fixed so as to cover as nearly as possible the cost of printing and distribution. The cost of preparing the index for the press is included in the editor's salary, and under the new arrangements its publication has been arranged for with an expedition hitherto impossible. From the number of Fellows who have applied and the number of copies which we may reasonably hope to sell to the public through our publishers, it seems probable that this volume of the Collective Index will not entail any serious outlay on the part of the Society.

The net income of the Research Fund for the year amounted to £367 6s. 5d., and by drawing on the balance in hand to the extent of £15 3s. 7d., grants were made amounting in all to £361, whilst the Longstaff Medal and Honorarium accounted for the remaining £21 10s.

A Vote of Thanks to the Treasurer, Secretaries, Foreign Secretary, and Council for their services during the past year, proposed by Mr. W. F. REID, seconded by Mr. A. CHASTON CHAPMAN, was acknowledged by Prof. ARTHUR W. CROSSLEY.

The PRESIDENT then delivered his Address, entitled, "The Walden Inversion." Sir WILLIAM TILDEN proposed a vote of thanks to the President, coupled with the request that he would allow his Address to be printed in the *Transactions*. The motion was seconded by Prof. HAROLD B. DIXON, and acknowledged by the PRESIDENT.

The Report of the Scrutators was presented, and the President declared that the following had been elected as Officers and Council for the ensuing year:—

President—W. H. Perkin, Sc.D., LL.D., F.R.S.

Vice-Presidents who have filled the office of President—H. E. Armstrong, Ph.D., LL.D., F.R.S.; A. Crum Brown, D.Sc., LL.D., F.R.S.; Sir William Crookes, O.M., D.Sc., F.R.S.; Sir James Dewar, M.A., LL.D., F.R.S.; H. B. Dixon, M.A., Ph.D., F.R.S.; P. F. Frankland, Ph.D., LL.D., F.R.S.; A. G. Vernon Harcourt, M.A., D.C.L., F.R.S.; Raphael Meldola, D.Sc., LL.D., F.R.S.; Hugo Müller, Ph.D., LL.D., F.R.S.; William Odling, M.A., M.B., F.R.S.; Sir William Ramsay, K.C.B., LL.D., F.R.S.; J. Emerson Reynolds, Sc.D., M.D., F.R.S.; the Rt. Hon. Sir Henry E. Roscoe, LL.D., F.R.S.; Sir Edward Thorpe, C.B., LL.D., F.R.S.; Sir William A. Tilden, D.Sc., F.R.S.

Vice-Presidents—H. Brereton Baker, M.A., D.Sc., F.R.S.; G. T. Beilby, LL.D., F.R.S.; H. T. Brown; LL.D., F.R.S.; E. J. Mills, D.Sc., LL.D., F.R.S.; G. T. Morgan, D.Sc.; W. Jackson Pope, M.A., F.R.S.

Treasurer—Alexander Scott, M.A., D.Sc., F.R.S.

Secretaries—Samuel Smiles, D.Sc.; J. C. Philip, M.A., D.Sc., Ph.D.

Foreign Secretary—A. W. Crossley, D.Sc., Ph.D., F.R.S.

Ordinary Members of Council—G. Barger, M.A., D.Sc.; E. J. Bevan; W. R. Bousfield, M.A., K.C.; A. J. Brown, M.Sc., F.R.S.; H. G. Colman, D.Sc., Ph.D; F. G. Donnan, M.A., Ph.D., F.R.S.; A. Harden, D.Sc., Ph.D., F.R.S.; T. M. Lowry, D.Sc.; H. Marshall, D.Sc., F.R.S.; K. J. P. Orton, M.A., Ph.D.; Sir Boverton Redwood, Bart., D.Sc.; E. J. Russell, D.Sc.

Anniversary Dinner.

The Anniversary Dinner of the Society was held at the Whitehall Rooms, Hotel Metropôle, on Friday, March 14, 1913.

The following toasts were proposed:—

By the PRESIDENT—"His Most Gracious Majesty the King." "Their Majesties the Queen and Queen Alexandra, His Royal Highness the Prince of Wales, and the other members of the Royal Family."

By the Right Hon. Lord Justice KENNEDY, P.C.—"The Chemical Society," coupled with the name of the President.

By Prof. W. H. PERKIN, LL.D., F.R.S., President-Elect of the Chemical Society—"Learned and Scientific Societies," coupled with the names of Sir Rickman J. Godlee, Bart., M.D., F.R.C.S, President of the Royal College of Surgeons, and Prof. E. B. Poulton, LL.D., F.R.S., President of the Linnean Society.

By Sir WILLIAM A. TILDEN, D.Sc., F.R.S., Past President of the Chemical Society—"The Guests," coupled with the names of the Right Hon. Lord Justice Hamilton, K.C., and Mr. H. G. Wells.

The Loyal Toasts having been honoured,—

Lord Justice KENNEDY, in proposing "The Chemical Society," said his one great regret was that he was truly and humbly conscious of his want of qualification to do justice to the toast. That disqualification was the absence of any knowledge of the great science which that Society had so successfully fostered and developed since its commencement in the year 1841. The necessities of his life had, unfortunately, compelled him to pursue a very different part from that of the study of the science which in the Chemical Society flourished and abounded. It was not often that law and science were so happily blended as they were in the case of the late Mr. Justice Grove, whose only regret, no doubt, after he was raised to the Bench was that he had not every day to study some case in which the most abstruse problem of chemistry would be presented for his judgment. It was the one drawback of an otherwise entirely enjoyable position. Their Society was, he understood, what he might call a voluntary college of research. They owed nothing to Governmental aid or interference. Nor was their primary aim the development of particular industrial success. Standing, as that Society did, in the position of a great leader, no thinking man could but recognise most gratefully the work that the Society had typified and strengthened. From Faraday to Frankland had been an epoch of chemical triumphs. They were not primarily, he understood, engaged in developing particular branches of chemical work, applied to what one might call practical ends, but a research society such as that guided, encouraged, and strengthened the individual development of special societies. During the last eighty or ninety years in this country there had been a re-formation and an improvement in every sphere of human life, owing to the marvellous discoveries of chemical science. It was difficult to find one field in which our life had not been made different by it. Whether we looked at sea or land, at intercourse, at industrial development, at the factory, or the workshop, or the farm, we saw what chemistry had done to make things better for those engaged in those industries. To the ordinary layman, like himself, we need only think one moment to realise that in our everyday life chemistry had made that life more comfortable and more enjoyable. Purer food, purer water, purer air, all the investigations and the successful investigations into the more mysterious causes of disease, which had provided a safeguard against some of the most frightful but, happily, as we now find, preventable causes of human misery—all these things were due to the development of chemical science. When we thought of all that, no one, he was sure, would fail to drink cordially the toast of the Society which embodied the research without which these particular improvements were impossible. The chemists might not have solved the problem which interested the alchemist of the Middle Ages. They might not have been able to find either the power of transmuting baser things into gold, or of finding the cure for old age and the discovery of eternal youth, but they had made by chemical

research, and by marvellous discoveries, life not merely more endurable but happier, and they had prolonged life not merely as a life, but as a working and enjoyable life. Further than that might he venture to say that to some of them, at any rate, there was the view that in the marvel lous possible discoveries which chemical science would bring to light we might be nearer the heart of the great mystery of all—life itself—we might be nearer the exploration of that mysterious borderland which lay between organic and inorganic matter; we might be nearer, possibly, the discovery of the truth: that things supposed now to be separated were closely allied, and the inner things—the powers of thought and imagination and the transference of both—might be explained in harmony with our knowledge and our aspirations. If, at any rate, that Society went on working in the spirit in which its leaders had always worked, in setting before themselves the purpose of working, simply and straightforwardly, to find the truth by experiment and observation, we should yet find that the harvest of thc past can be exceeded by the harvest of the future. They all believed that there lay before a Society like that, leadership in the search for truth in one of the most important realms of nature; and if the spirit of the past remained with those who worked in the future, they might be able, when assembling, as they were then doing, at some future date, to chronicle success of which that night they dare not dream—success which would have a real value, not merely in the material prosperity of our country, but in the development of the truth, for which all so earnestly longed, with regard to secret things as yet but guessed at. They knew that in many places in Scotland and in England their Chairman had done most valuable work, both as a searcher after truth and as a great and successful contributor to the material value of chemical science. When one looked at what he had done, one could see in him the embodiment of that Society, which worked for research, but which was never happier than when that research and the discovery which followed it were able to contribute to the practical happiness and the welfare of the community.

The PRESIDENT said it had been a great gratification to him to hear his Lordship speak not only with such appreciation of the Chemical Society, but also in such kindly terms of himself. The proposer of the toast referred to the Chemical Society from the outside. Perhaps he might be permitted to say a few words about the Society from the inside. The Society was the oldest chemical society in the world, and although they had now exceeded the age of three-score years and ten, he did not think they exhibited much of the decrepitude associated, often most erroneously, with advanced age. He did not propose to boast of the age of their Society, which was nothing if not progressive. It was far better to see how they stood and were likely to stand in the future than to dwell overmuch on the glories of the past. He thought they might be assured of this: that they numbered amongst their living Fellows several great masters who could count amongst their exploits what were undeniably some of the most brilliant discoveries that had ever been made by man. Nor need they fear for the future prestige of their Society when they saw an ever-increasing enthusiasm for research among the younger generation of their Fellows who were gaining distinction, many of them, in every branch of chemical science. But the progress of chemistry did not depend solely upon the efforts of their Fellows, for whilst during the past twenty years so many chemists had become physicists, quite recently the tables had been turned, and physicists were becoming chemists. That eminent physicist, Sir Joseph Thomson, had entered the field of analytical chemistry, and had invented an absolutely new system of chemical analysis. There was also Prof. Strutt, with his "active nitrogen," whilst Prof. Rutherford, in his wonderful researches on radio-activity, had revealed the existence of a whole series of new elements. Those eminent physicists had discovered, what chemists had long known, that the science was the most exacting of mistresses, making more imperious demands on the time and patience of her votaries than any of her sisters. Chemistry was also the science of which the aim, scope, and method were least understood, not only by the general public, but by that august assemblage of persons who styled themselves "the cultivated classes." Owing to this widespread absence of knowledge of chemistry—to which the proposer of the toast had pleaded guilty—the public were particularly liable to be misled by sensational statements which appeared from time to time in the Press. Only a few short months ago they were credited with being on the eve of the discovery of the synthesis of life itself; and still more recently there was the startling announcement that chemists were now able to manufacture matter out of ether or out of electricity. He did not think they had any cause to complain of the position they filled in the public eye when such divine powers as these were ascribed to them. They had proverbial authority for saying that where there was smoke there was fire, and the mere fact that such statements were made showed how far they had travelled since the Society was founded seventy-two years ago. They had indeed, during recent years, made astounding strides in their knowledge of the chemistry of life, and had also come to extraordinarily close quarters with the atoms and molecules of which matter was made up. When they considered that accurate and systematised chemical knowledge only went back for a little over one hundred years, what might not another century of investigation bring forth? It used to be a favourite theme, and a favourite practice with past Presidents of the Society to refer to the lack of encouragement given to investigators in this country, and to point out the indifference and apathy of our rulers towards science and matters connected with science in general. He did not think that subject required labouring, for he believed everyone present would agree, after the object lessons we had had, that there could be no sort of doubt as to what was likely to be the fate of any country in which science was persistently neglected and treated in a step-motherly fashion. Some years ago a society was formed for the sole purpose of impressing on those in authority how great were the perils which surrounded their self-complacent indifference towards matters connected with science. He was sure the Chemical Society wished all success to the British Science Guild, which had taken upon itself that difficult and Sisyphean task. Regrettable as, no doubt, was the attltude of our actual rulers towards most matters connected with science, there were signs that our would-be rulers were turning their attenlion to chemical phenomena. More especially in those attacks which now imperilled our correspondence —and which, he had reason to believe, had led to several invitations to that dinner failing to reach their destinations —they had read of the employment of a spontaneously inflammable liquid, the first accounts of which suggested that some subtle organic chemical – possibly zinc methyl— was being employed by these hysterical and deluded malefactors. It was therefore a relief to learn that more accurate investigation showed that no such profound knowledge of chemistry was involved, but that only phosphorus, the properties of which a learned judge and jury had declared to be the common knowledge of every schoolboy, was being degraded to such nefarious and deplorable uses. It was this abuse of chemical knowledge in all ages which had sometimes led to the belief that chemists were working in partnership with the Prince of Darkness himself. But their Society could not be charged with being privy to any such sinister acts, because it was not concerned with any of the applications of chemistry, but only with the progress of chemical knowledge. The progress of chemical knowledge they assisted by means of their scientific meetings, their Research Fund, and especially by means of their publications, which consisted of volumes of *Transactions*, *Proceedings*, Abstracts, and Annual Reports, the whole constitutfng a living record of chemical discovery from year to year. Just as they were the pioneers in the formation of a chemical society, so they had been the pioneers

in eertain matters connected with scientific publication. He believed they were the first society to supply abstracts of all publications of chemical interest throughout the world. Their annual reports, again, had been of priceless value to their Fellows. He believed he was right in supposing that chemical literature was more perfectly organised than the literature of any other science, and that their nomenclature transcended in clearness of language and terseness anything that had yet been invented. But chemists had determined further to improve their nomenclature, and the labours of the International Association of Chemical Societies would be very greatly lightened if they could accept the opinion of that eminent French physical chemist, M. Le Chatelier, who had asserted that he did not believe that more than a small fraction of the so-called organic compounds had any existence whatsoever excepting in the imagination of their alleged discoverers. It would appear that the great obstacle with which the progress of science was destined to be confronted in the future was the impossibility of integrating the immense amount of knowledge gained by individual investigators. There was much evidence that even the ablest men in one branch of science were often quite unable to form a clear and sound understanding of what another branch were engaged in. For that, it would appear, they must wait for some chance mutation in the evolution of the human faculties which would provide them with some superman capable of co-ordinating and utilising the enormous wealth of information and knowledge which had been accumulating in the separate and almost water-tight compartments into which science had now become divided, and in which the several groups of investigators were working in close and solitary confinement. He concluded by expressing regret at the loss by death during the past year of Dr. Divers, who was the apostle of modern chemistry in the Far East, and of Dr. Wade and Dr. Jones, who were struck down under such tragic circumstances. He thanked the Society for the great honour they had conferred upon him in permitting him to occupy the Chair which had been filled by such eminent predecessors. They all wished Prof. Perkin (the President elect) not only success in the Presidential Chair, but also a long and brilliant career in the Chair to which he had so recently been called in the University of Oxford.

Prof. W. H. PERKIN proposed "Learned and Scientific Societies." He said members of the Chemical Society had always gratefully recognised the results of the work of other learned societies in so many branches of science, and he thought it might well be said that every learned society reacted on and stimulated the other learned societies. Chemists owed a debt of gratitude to the Royal and Chemical Societies, more especially for the financial assistance received in connection with their investigations, and without which many of their researches could hardly have been attempted. They hoped that wise and generous donors would be found in the near future who would augment the insufficient funds at the disposal of the learned societies, and would thus enable them to do still more for research.

Sir RICKMAN J. GODLEE, in response, said in the last fifty years chemistry had made strides at least as great as those of his profession, and surgeons were almost, if not quite, puzzled by the number of new substances, drugs, and chemical compounds that were being launched upon them. Radium, he supposed, was the substance beyond all the rest which had given rise to great searching of heart amongst them. In their treatment by radium they were met by the most irregular results, and they must wait and hope that more would be known about it in the future. He expressed the opinion that chemical nomenclature very much confused the medical student.

Prof. E. B. POULTON also briefly acknowledged the toast.

Sir WILLIAM A. TILDEN proposed "The Guests."

Lord Justice HAMILTON, in response, said he belonged to a profession which occupied its time in peering, with blear-eyed gaze, into the work of those in the past who framed immutable laws for the government of the present. We had come to the time, however, when we appreciated that the laws of England changed remarkably fast, and it was some consolation to know that the laws of science, in the hands of chemists, appeared to be passing through the same change. Although the guests came there, representing every possible occupation and unanimous in their sympathy with chemistry, and interested with chemists in their sacrifices for science, he did not suppose that the members of the Chemical Society quite recognised how little the outsider knew about chemistry, and sometimes how little he cared about it. He himself was once being coached in one of the ologies, for the purpose of a case, and he found in the proof of one of his experts something about molecules. So he said to the learned gentleman who was assisting him, "What are molecules?" He replied, "They are just a term we use when we are talking about what we don't understand." A great deal had been said about the importance of chemistry to the human race, and about the blessings it had conferred on the human race. But was it not a fallacy to suppose that chemistry existed for the improvement of the human race, or that the desire of the chemist was to benefit mankind? Of course, the chemist desired to keep his wife and family in comfort, but what concern had he with the human race at large? Was it his business to make chemical champagne or chemical cheese? What the chemist wanted was not to improve the human race, but to know more chemistry. Incidentally he believed that if they knew more and more chemistry, it did more good to other people. He ventured to suggest that the attitude of the true chemist towards the improvement of this human race might be expressed in the language a noble lord once used with regard to "the consequences." His business was not to invent new forms of pure air or pure water, or complications of that kind. His business was to know more, to add to the sum of human knowledge, and if he then passed away into the infinite he would know the unknowable, and with that he would be content.

Mr. H. G. WELLS also replied. He complained of the obscurity that had fallen upon the atom since his student days. He said he wished chemists would make things clearer to those who lived in the darkness outside their Society. He could not help asking: Did they realise how wonderful a thing their science was? Science to him had always been the true romance. The beleaguered castle and the beautiful damsel had always seemed to him small incidental stuff beside the great fantasia of scientific possibilities. Again and again in his novels he had tried to make the scientific man his hero. Did they realise that science, as we understood it, was a new thing? It was something absolutely new in human affairs. In the last 200 or 300 years it was something which had been added to human life, something which gave permanent results, and was continually growing. There was only a little band of men who were doing this scientific work and adding to this strange new body of knowledge, a band which numbered, at a generous estimate, considerably less than five thousand. And yet that little band, it appeared to him, was rapidly changing all the conditions of human life. Discussing the effect of chemistry upon war, Mr. Wells said that during the last thirty years the whole of Europe had been arming, and chemists had been putting weapons into the hands of the warrior. And now the warrior, armed with the weapons which they chiefly had given to him, was afraid to let them off because he realised that he would blow the whole fabric of civilisation to pieces. Chemists had not, perhaps, made war impossible, but they had made it preposterous. Almost at any time, too, chemists might be flinging great chunks of synthetic gold into a world, whose whole economic order might be upset by the feat. When he thought of all these things his admiration for their work tottered into a kind of terror. He felt that either this rapid alteration of every material condition of life must stop, or else other things, economic ideas, social ideas, legal conceptions, must rouse themselves to keep pace with it.

PHYSICAL SOCIETY.

Ordinary Meeting, April 11th, 1913.

Prof. C. H. Lees, F.R.S., Vice-President, in the Chair.

A paper "*On Errors in Magnetic Testing Due to Elastic Strain*," by Mr. A. Campbell and Mr. H. C. Booth, was read by Mr. Campbell.

In magnetic tests on sheet material considerable errors may occur if the sheets or strips are tested while in bent form. These errors, which are in general agreement with the known effects of compression and tension, were investigated experimentally with one or two forms of magnetic circuit similar to those sometimes occurring in practice. In one method a single length of the strip was bent into ring form with ends clamped together. This was wound with flexible primary and secondary coils, and tested for permeability and hysteresis, while in the condition of temporary strain. The temporary strain was then annulled by changing the circular form into a square by sharp bends at four places. The magnetic tests were repeated, and usually a considerable alteration was observed. For example, a silicon-iron ring 0·3 mm. thick and 50 cm. in diameter (the size used in Richter's method of testing hysteresis and eddy current losses) showed a decrease of 40 per cent in the permeability for H = 1 due to the bending. The hysteresis loss was increased by 19 per cent. In another method the ends of two strips were clamped in yokes, and tests were made with different amounts of bending. It was found that temporary strain has considerably greater effect on the permeability than equal permanent strain has.

Prof. C. H. Lees pointed out that the authors had not clearly distinguished between the effects of stress and strain, and that the results would be more intelligible if this distinction were made. The condition called by them "temporary strain" was strain plus stress, while that called "equal permanent strain" was the strain without the stress. From the point of view of the molecular dynamical theory he thought the effects of stress ought to be separated from those of strain.

Dr. S. W. J. Smith expressed interest in the results, and, referring to the difference between the effects produced by temporary stress and by permanent strain, thought there was no reason to expect any simple relation between them. Under different fields, in the same material, or under similar fields, in other materials, the effects might even be opposite to one another in sign.

Prof. T. Mather asked if the sheets were ever annealed after being bent, before testing them by Richter's method, as this would seem to remove the objections against the method.

Mr. A. Campbell, in reply, admitted the advisability of separating the effects of stress from those of strain. The advantage claimed for Richter's method was that it in no way mutilated the sheets. If they were annealed after they were bent into a cylinder this advantage would be destroyed.

A "*Note on Cathodic Sputtering*" was read by Dr. G. W. C. Kaye.

The paper gives an account of the volatilisation of an aluminium cathode in a discharge tube containing helium. The sputtered deposit on the glass indicates that, under the conditions which prevailed, the disintegration was restricted to the edges of the cathode and did not occur elsewhere. Accordingly the complete outline of the cathode (made by rolling a sheet of aluminium into a nearly complete cylinder) was traced out by the deposit on the walls of the tube.

Prof. J. W. Nicholson asked if the size of the particles bore any relation to the atomic weight of the metal.

Prof. T. Mather asked if Dr. Kaye had made any tests of the conductivity of the films, and whether they obeyed Ohm's Law.

Mr. D. Owen inquired how adherent the films were to the glass.

The Author, in reply, stated that the size of the particles depended chiefly upon the nature of the gas in the tube. The method had been considerably used for preparing extremely high resistances, though the film had to be annealed first. He believed the thinnest films did not accurately obey Ohm's Law. The adherence of the film varied with the metal. Gold adhered to glass well, but platinum was easily rubbed off till it had been heated to redness.

A paper on "*Vibration Galvanometers with Unifilar Torsional Control*" was read by Mr. A. Campbell.

The author exhibited a moving coil vibration galvanometer in which a novel principle is used to obtain the fine adjustment of the control torque requisite for accurate tuning. He has found that in a phosphor bronze strip under tension the torsional rigidity is considerably increased as the tension is raised. This anomalous behaviour of such strips has also been noticed by other observers (H. Pealing, *Phil. Mag.*, March, 1913). If unifilar (strip) suspensions are used in a vibration galvanometer (whether of moving-coil or moving-iron type) the tuning can be done in just the same way as with bifilar suspension. In the moving-coil instrument minute hooks on the ends of the strips engage in contact hooks at the top and bottom of the coil, which is easily detachable.

With a mirror of 15 sq. mm. area, at 100 vibrations per second, a sensitivity of 50 mm. at a metre per microampère can be obtained, the effective resistance being about 700 ohms.

Prof. T. Mather asked Mr. Campbell if he did not think the variation of period was possible because of the bifilar behaviour of a flat strip.

Prof. C. H. Lees remarked that it seemed natural to expect a strip to behave like a bifilar. He thought Pealing's dismissal of this explanation rather too summary.

The Author, in reply, stated that to some extent the result must certainly be due to bifilar behaviour. The effect due to this cause decreased as the length of the strip increased. In his own case, where the length was only about 1 cm., it was probably large, but he did not think that this could be the whole explanation of the results in Pealing's experiment, where a length of 40 cm. was used.

Conference of Technical Teachers.—The annual conference of the Association of Teachers in Technical Institutions will be held this year in Bradford at Whitsuntide. The proceedings will be opened on Whit Monday, when the Lord Mayor of Bradford, Alderman Fred Foster, will officially welcome the conference to Bradford. This will be followed by the address of the President, Mr. P. Coleman, of the Northern Polytechnic Institute. The meeting on Tuesday evening will be addressed by the Right Honourable J. A. Pease, President of the Board of Education, and in view of the introduction of the new Education Bill soon after Whitsuntide, this address will be looked forward to with exceptional interest. This meeting will also be addressed by Michael E. Sadler, C.B., Vice-Chancellor of the University of Leeds; Sir William Priestley, M.P.; Sir Alfred Keogh, K.C.B.; Rector of the Imperial College of Science and Technology, F. W. Jowett, M.P., and others. Papers will be read to the conference on "Corporate Life in a Technical Institution," by W. Hibbert, the Polytechnic, Regent Street; "Vocational Education, by A. C. Coffin, Director of Education, Bradford; and "Co-ordination within a County Area," by F. N. Cook, Secretary for Higher Education in the West Riding of Yorkshire. A special service has been arranged in the Parish Church for Whit Sunday and a Conference Sermon will be preached by the Bishop of Ripon.

NOTICES OF BOOKS.

Steam Economy in the Sugar Factory. By KARL ABRAHAM. Translated from the German Edition by E. J. BAYLE. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1912.

THE translator of this book, who has had much experience in the organisation of beet- and cane-sugar factories, believes that it is the best on the subject extant, and has rendered it into English in the hope that engineers, sugar works' managers, &c., may find it useful. The translation is very literal, and the German idiom has been closely followed; all German weights and measures have, however, been converted into the English equivalents. An outline of the process of elaborating white crystal sugar is first given, and a thoroughly practical discussion of the steam consumption of individual stations, and the factors influencing it, follows. The question of the distribution of steam and steam economy is then fully treated. A great number of carefully worked out and explained numerical examples is included, and the book contains many tables and is partially interleaved with squared paper.

Explosives. By Dr. H. BRUNSWIG. Translated and Annotated by CHARLES E. MUNROE, Ph.D., LL.D., and ALTON L. KIBLER, M.S., Ph.D. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1912.

IN this book the literature of explosives is very thoroughly summarised and criticised, and while it lays special stress on the development of the theory of explosives from the point of view of physical chemistry, the technologist will no doubt find that it throws fresh light upon many of the problems with which he has to cope. The general behaviour of explosive systems is first treated, and the velocity of reaction and explosion temperature and pressure are discussed in considerable detail, although the mathematics which are introduced are made as easy and elementary as possible. The individual explosives are then discussed in turn; both English and foreign methods of manufacture are included for description, and very clear and concise summaries are given of the properties of the different types. The translators have added some notes giving the results of their own experiments or pointing out slight differences of detail in German and American practice.

Concrete and Constructional Engineering. Volume VIII., No. 2, February, 1913.

IN the February number of *Concrete and Constructional Engineering* some notes are given on the opening of the Assouan Dam, and cases of failure of reinforced concrete are discussed in the Editorial. Among the papers included in the issue are one on the extension of Siemens, Bros., and Co.'s Works, Woolwich, and another on the recently built reinforced concrete wharf and jetty at Saint Louis, Sénégal, both of which are fully illustrated. A paper read by Mr. W. Lawrence Gadd before the Concrete Institute on the "Action of Acids, Oils, and Fats upon Concrete" is published in the Journal, with an abstract of the discussion which followed it.

Das Erdöl. ("Petroleum"). By C. ENGLER and H. v. HÖFER. Vol. I., Part II., with Tables. Leipzig: S. Hirzel. 1913.

IN this second part of Volume I. of Engler and v. Höfer's comprehensive text-book on petroleum the continuation of the section on the chemistry of petroleum is given, including the full discussion of the characteristics of oils of various origins. The properties and chemical behaviour of allies of petroleum, namely, asphalt, ozokerite, natural gas, &c., are also treated, and an account is given of the physiological action and the medicinal use of petroleum. The tables, which are not printed in the text, but are enclosed in a case, give on sheets measuring 21 by 37 inches the results of the analysis of many petroleums as well as the results of the determination of rotatory power.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Bulletin de la Société Chimique de France. Vol. xiii.-xiv., No. 3, 1913.

Phenyl-stibines.—P. Carré.—The best way to prepare the phenyl-stibines is to allow phenyl magnesium bromide to act on antimony trichloride. When a small quantity of organic magnesium derivative is used the chief product is triphenyl-stibine, while when 1 or 2 molecules of organic magnesium compound are employed to 1 molecule of antimony trichloride the chlorides of mono- and diphenyl-stibine, $C_6H_5SbCl_2$ and $(C_6H_5)_2SbCl$, are formed, as well as triphenyl-stibine. The two chlorides are decomposed by heat, giving triphenyl stibine and antimony trichloride.

Colour Reactions of Chlorates. — J. Pieraerts.—Lafitte has pointed out that chlorates can be detected by the formation of a violet-red coloration, turning to blue, when an aqueous solution of aniline and fuming hydrochloric acid are added. The author finds that the best proportions to use are 5 cc. of 2·5 per cent aniline and 6 cc. of fuming HCl to 1 cc. of 1 per cent $KClO_3$. The use of alcoholic aniline solution greatly increases the sensitiveness of the reaction, while the presence of iodates vitiates it altogether.

Determination of Reducing Sugars by Lehmann's Method.—L. Grimbert.—Lehmann's method of estimating glucose consists in determining the excess of copper which remains in cupropotassic liquid after it has been reduced by the sugar. The copper is titrated with potassium iodide solution, 1 atom of iodine being liberated by 1 atom of copper. Various authors have suggested modifications of this method, but of all of their processes only that of Bertrand (*Bull. Soc. Chim.*, xxxv., 1285) is reliable, and if his directions are exactly followed very accurate results may be obtained.

MEETINGS FOR THE WEEK.

MONDAY, 28th.—Royal Society of Arts, 8. (Cantor Lecture). "Antiseptics and Disinfectants," by David Sommerville.

TUESDAY, 29th.—Royal Institution, 3. "Recent Physiological Inquiries—Motion and Locomotion," by Prof. W. Stirling, M.D., &c.

WEDNESDAY, 30th.—Royal Society of Arts, 8. "The Science Museum," by F. G. Ogilvie, LL.D.

THURSDAY, May 1st.—Royal Institution, 3. "The Progress of Hittite Studies—Cults of Northern Syria," by Prof. John Garstang, M.A., &c.

— Royal Institution, 5. Annual Meeting.

— Royal Society. "Capacity for Heat of Metals at different Temperatures," by E. H. and E. Griffiths. "Transition from the Elastic to the Plastic State in Mild Steel," by A. Robertson and G. Cook. "Studies of the Processes Operative in Solutions—XXVIII., Influence of Acids on the Rotatory Power of Cane-sugar, of Glucose, and of Fructose," by F. P. Worley. "Attainment of High Potentials by the Use of Radium," by H. G. J. Moseley. "Decrease in Velocity of α-Particles in passing through Matter," by E. Marsden and T. S. Taylor.

— Chemical, 8.30. "Di-naphthathioxin and Iso-di-naphthathioxin," by T. J. Nolan and S. Smiles. "Bismuthinitrites," by W. C. Ball. "Constitution of Aliphatic Diazo-compounds," by M. O. Forster and D. Cardwell. "Estimation of Zinc as Zinc Ammonium Phosphate and Zinc Pyrophosphate," by T. M. Findlay and A. C. Cumming. "Condensation of Acetonedicarboxylic Acid with Phenols," by B. B. Dey. "Oxidation of Sphingosin," by A. Lapworth. "Conversion of Sodium Hydrosulphide into Sodium Monosulphide," by J. S. Thomas and A. Rule. "Influence of Temperature and Pressurs on the Rate of Volatilisation of Zinc and of Cadmium," by T. K. Nair and T. Turner. "Constitution of Oxydiazole Oxides (Furazane Oxides or Dioxime Peroxides," by A. G. Green and F. M. Rowe. "Constitution of Furoxans (Dioxime 'Peroxides')," by M. O. Forster and M. F. Barker.

FRIDAY, 2nd.—Royal Institution, 9. "Blood Parasites," by Henry G. Plimmer, F.R.S., &c.

SATURDAY, 3rd.—Royal Institution, 3. "Chaucer," by Prof. Sir Walter Rayleigh, M.A.

THE CHEMICAL NEWS.

Vol. CVII., No. 2788.

SOME QUANTITATIVE SEPARATIONS OF NEODYMIUM.

By T. O. SMITH and C. JAMES.

During the separation of the crude rare earths as oxalates from acid solutions of minerals, it has been observed that varying amounts of other elements, such as titanium, uranium, &c., accompany the precipitate. It therefore seemed advisable to study this matter from the quantitative standpoint. Neodymium was chosen because it so happened that plenty of pure material was at hand; and, also, because of its position in the series, it would seem to give results that would be in accord with the other members of the group.

A standard neodymium chloride solution was prepared from the pure oxalate in the following manner:—The oxalate was ignited to the oxide, Nd_2O_3, in a weighed platinum dish, and the exact weight of the oxide found. It was then carefully dissolved in a slight excess of hydrochloric acid, and the excess of the latter removed by gentle evaporation to dryness. The salt so obtained was dissolved in water diluted to a known volume, and the strength of the solution calculated.

This standard solution was then further checked by measuring out 50 cc., diluting, heating to boiling, and precipitating with oxalic acid. The precipitated oxalate was allowed to stand an hour, washed with cold water, dried, and ignited to the oxide. This showed that the solution contained 0·002876 grm. Nd_2O_3 per cc. It was found to check perfectly with the calculated result. A standard neodymium chloride solution might therefore be prepared by simply dissolving a known weight of the oxide in the required amount of hydrochloric acid and diluting to the desired volume.

Separation of Titanium.

To prepare a standard titanium solution dry titanium dioxide was treated with hot sulphuric acid, forming basic titanium sulphate, $(TiO)SO_4$. Any considerable excess of acid was evaporated off. The granular white mass of basic sulphate was put into solution by repeated decantations with dilute sulphuric acid. The final solution contained about 4 cc. of concentrated sulphuric acid per litre. This amount of acid, however, was not sufficient to hold the titanium in solution for a very great length of time. The solution was standardised by precipitating with ammonia and weighing as titanium dioxide. It was found to contain 0·003174 grm. TiO_2 per cc.

To effect the separation, the standard solutions of neodymium chloride and basic titanium sulphate were poured with stirring into a boiling oxalic acid solution. At first a voluminous precipitate was formed which soon became granular upon digesting at about 100° with occasional stirring. The granular precipitate filtered well, and was thoroughly washed with a cold 5 per cent oxalic acid solution, and finally with water. The data are given in Table I.

An attempt was made to separate titanium from neodymium by the following procedure:—The mixed solutions were precipitated by ammonia and the hydroxides carefully washed with hot water. They were then treated with dilute nitric acid. The solution was evaporated to dryness on the water-bath, and the free acid driven off in the air-bath at 105°. The neodymium was then taken up with hot water while the titanium was left behind. In view of the results obtained, as well as the amount of time and work involved, this method is not to be recommended.

Table I.

No. of sample.	TiO_2 taken. Grm.	Nd_2O_3 taken. Grm.	Nd_2O_3 found. Grm.
1.	0·1587	0·1438	0·1437
2.	0·1587	0·1438	0·1437
3.	0·07935	0·1438	0·1432
4.	0·1587	0·1438	0·1416
5.	0·23805	0·1438	0·1437
6.	0·1587	0·1438	0·1438
7.	0·1587	0·1438	0·1438
8.	0·07935	0·1438	0·1439
9.	0·1587	0·1438	0·1437
10.	0·23805	0·1438	0·1407

Separation of Glucinum.

A glucinum nitrate solution was standardised by precipitating the hydroxide with ammonia and igniting to the oxide. It was found to contain 0·003824 grm. GlO per cc. The glucinum and neodymium salts were mixed in dilute solution, heated to boiling, and the neodymium precipitated by the addition of a slight excess of oxalic acid. The oxalate was washed with cold water and weighed as the oxide. The data are given in Table II.

Table II.

No. of sample.	GlO taken. Grm.	Nd_2O_3 taken. Grm.	Nd_2O_3 found. Grm.
1.	0·0956	0·1438	0·1438
2.	0·1912	0·1438	0·1436
3.	0·2868	0·1438	0·1438

Separation of Uranium.

A standard uranium solution was prepared by the method of precipitating hydrated ammonium uranate from a uranyl solution and igniting to uranoso-uranic oxide. The salt used was uranyl nitrate, $UO_2(NO_3)_2$, and the solution prepared contained 0·001208 grm. U_3O_8 per cc.

Varying amounts of this solution together with the standard neodymium solution were diluted to 250 cc. and heated to boiling. The neodymium was precipitated by the addition of a slight excess of oxalic acid. The solution was kept hot for about fifteen minutes to allow the voluminous precipitate to become granular. It was then set aside for a half-hour, or longer, after which it was filtered, ignited, and weighed. The data are given in Table III.

Table III.

No. of sample.	U_3O_8 taken. Grm.	Nd_2O_3 taken. Grm.	Nd_2O_3 found. Grm.
1.	0·0604	0·1438	0·1440
2.	0·1208	0·1438	0·1439
3.	0·1812	0·1438	0·1440

Separation of Barium.

A standard barium chloride solution was prepared by the usual method of precipitating and weighing the sulphate. The neodymium was separated as the oxalate as in previous cases, and the barium in the filtrate also estimated. The data are given in Table IV.

Table IV.

No. of sample.	$BaSO_4$ taken. Grm.	Nd_2O_3 taken. Grm.	$BaSO_4$ found. Grm.	Nd_2O_3 found. Grm.
1.	0·0900	0·1438	0·0900	0·1432
2.	0·1800	0·1438	0·1799	0·1430
3.	0·2700	0·1438	0·2697	0·1433

Separation of Zirconium.

Zirconium oxychloride was dissolved in water to which had been added a few drops of hydrochloric acid to keep it in solution. By precipitating the hydroxide with ammonia and igniting to the oxide this solution was found to contain 0·004156 grm. ZrO_2 per cc. A measured portion of this solution together with the neodymium chloride was diluted to 250 cc. and heated to boiling. Since zirconium oxalate is insoluble in water, but is soluble in oxalic acid, the precipitant was added in considerable excess. After holding at about 100° for a few minutes it was allowed to stand for some time at ordinary temperature. It was then filtered, washed with 5 per cent oxalic acid, and finally with water. The data are given in Table V.

TABLE V.

No. of sample.	ZrO_2 taken. Grm.	Nd_2O_3 taken. Grm.	Nd_2O_3 found. Grm.
1.	0·1039	0·1438	0·1448
2.	0·2078	0·1438	0·1449
3.	0·3117	0·1438	0·1452

The above results indicate that a little zirconium is carried down. They could probably be lowered by adding the mixed chlorides to the boiling solution of oxalic acid, since this would prevent the formation of the insoluble zirconium oxalate.

Durham, New Hampshire, February 27, 1913.

CONTRIBUTION TO THE THEORY OF INDICATORS.

By JOHN WADDELL, D.Sc., Ph.D.

THE theory of indicators is not in a satisfactory condition. Lunge ("Technical Methods of Chemical Analysis," p. 53) says that indicators are usually divided into three classes, those which are only slightly sensitive to weak acids, such as methyl-orange; those of medium sensitiveness, such as litmus; and those which are almost as sensitive to the weakest as to the strongest acids, such as phenolphthalein. The first class of indicators are comparatively strong acids, the second not so strong, and the third very weak indeed.

Since acids and bases are the complement of each other it is not to be expected, *a priori*, that all indicators should be acid. There would seem to be as much probability that a coloured base might act as indicator as a coloured acid. It is strange, too, that methyl-orange, a strong *acid*, should act towards weak *acids* in exactly the same way as phenolphthalein, a weak *acid*, acts towards weak *bases*. It would not be strange if methyl-orange, a weak *base*, should act towards a weak *acid* in a manner similar to that of phenolphthalein, a weak *acid*, towards a weak *base*; and I shall present a theory of indicators which seems to me to correspond to the facts, and which would explain the action of methyl orange as well as that of phenolphthalein. According to this theory, methyl-orange is a weak *base*, not a strong *acid*. I am not aware of any reason why methyl-orange should be considered an acid, except for the presence of the sulphonic group, but set over against this group is the amino group giving a basic character, which is accentuated in the sodium compound.

According to the received theory of electrolytic dissociation, strong alkalis and acids are largely dissociated, but weak alkalis like ammonia, and weak acids like acetic acid, are but slightly dissociated. Ordinary ammonium salts, however, are nearly as much dissociated as the corresponding sodium salts, and sodium acetate is nearly as much dissociated as sodium nitrate or chloride in equivalent solutions. Indeed, ammonium acetate in aqueous solution is very considerably dissociated.

With very weak acids, however, hydrolytic dissociation plays a prominent part, electrolytic dissociation becoming less. This is the case with sodium carbonate, and ammonium carbonate is apparently still more hydrolysed with correspondingly less electrolytic dissociation.

Phenolphthalein is a still weaker acid than carbonic, and the ammonium salt has still less electrolytic dissociation, which dissociation may be diminished by the addition of other largely dissociated ammonium salts, such as the chloride. When phenolphthalein has been just reddened by the addition of ammonia, the colour may be discharged by the addition of sufficient solid ammonium chloride. If dry phenolphthalein is added to even a cubic centimetre of the strongest ammonia solution the red colour may be almost removed by the addition of solid ammonium chloride. The undissociated phenolphthalein is therefore colourless, and the dissociated anion is red. If this is the case any other method which would lessen dissociation should lessen the colour. Organic solvents in general give rise to less dissociation than water does, and if a few cubic centimetres of alcohol or ether are added to phenolphthalein, reddened by a cubic centimetre of the most concentrated ammonia solution, the colour is completely discharged, but may be brought back again by the addition of water, and, if too much water has not been added, again discharged by alcohol or ether.

Phenolphthalein is on all hands admitted to be a weak acid; it is generally admitted that the red colour is due to the ion (probably with some molecular rearrangement), and that the colourless compound is undissociated. In the case of methyl-orange, if it is an acid the pink colour is due to the undissociated molecule, and the yellow to the dissociated anion, because the yellow in methyl-orange corresponds to the red in phenolphthalein.

All means of diminishing the dissociation, however, tend to change the colour from pink to yellow. Glacial acetic acid to which methyl-orange is added gives a red colour, which may be lessened, if not destroyed, by the addition of acetates, and which is easily changed to yellow by the addition of alcohol. This is easily understood if methyl-orange is a weak base, because the salt formed with acetic acid is only slightly dissociated, and that dissociation can be easily overcome, producing the yellow compound. The yellow colour is therefore that of the undissociated compound, and the red is due to the dissociated *cation*. Carbonic, boric, and silicic acids are so weak that even in aqueous solution methyl-orange does not form dissociable salts, and therefore has a yellow colour.

With a strong acid like hydrochloric it is not easy to overcome the dissociation, but if to a drop of the most concentrated hydrochloric acid solution dry methyl-orange is added, the red colour can be largely removed by alcohol, and, though I have not tried the experiment, I think there is no doubt that if almost dry hydrochloric acid gas were passed through an alcoholic solution of methyl-orange, the colour would remain yellow. Even those who consider methyl-orange a stronger acid than acetic are not likely to place it ahead of hydrochloric, as would need to be the case if the yellow colour of methyl-orange were due to the dissociated anion.

As we have substances, such as aluminium hydroxide,* which act both as bases and acids, so there are indicators which have both functions. Fluorescein and phenacetolin belong to this number which are not very sensitive to very weak bases or to very weak acids. Phenacetolin, for example, gives a red colour in alkaline solution and yellow in acid, but if the alkali is ammonia the red colour can be changed to pale pink by alcohol or acetone; and if the acid is acetic, the yellow colour can also be changed to pale pink by the same reagents. From this it appears that the undissociated compound is pale pink, the anion is red and the cation yellow (see *Note*).

(NOTE.—Some expressions in Prof. A. A. Noyes's explanative paper on "Indicators," *Journ. Am. Chem. Soc.*, xxxii., 815, indicate the same view as that briefly given here, but I venture to submit this mode of presentation).

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* It may be that aluminium hydroxide is not amphoteric, but as has long been considered so it is used as an illustration.

THE TESTING OF SAFETY EXPLOSIVES.*

By Prof. VIVIAN B. LEWES, F.I.C., F.C.S., &c.

(Concluded from p. 195).

Reading through the percentage prescriptions for the explosives on the permitted list, it soon becomes apparent that one large class of safety explosives has been arrived at by cooling down the explosion of nitroglycerin by adding cellulose in various forms and in sufficient quantity to ensure the formation of products of incomplete combustion, and then adding diluents of a character likely to stifle flame; whilst a second class has been formed by the reverse process of "waking up" ammonium nitrate by adding 4 or 5 per cent of nitroglycerin or trinitrotoluene to it to ensure complete detonation, and then further cooling by replacing some of the ammonium nitrate by sodium or potassium nitrate with or without other diluents. A third class consists of trinitrotoluene or other nitro-substitution products, with oxidising salts, generally nitrates of potassium, sodium, and ammonium, and diluents.

As examples of these three classes in their simplest form, we may take:—

1. *A Wetter Dynamite.*

Nitroglycerin	44
Cellulose	12
Sodium sulphate	44

2. *Densite* III.

Trinitrotoluene	4
Ammonium nitrate	74
Sodium nitrate	22

3. *Densite* IV.

Trinitrotoluene	19·0
Ammonium nitrate	18·0
Potassium nitrate	45·5
Ammonium chloride	17·5

The marked characteristic that is to be found in the products of combustion evolved by the first class is that they contain large volumes of carbon monoxide, whilst the products from the second class and from some explosives in the third class contain free oxygen, often in considerable quantities. Already it has been recognised at Rotherham that all explosives do not behave alike in both gas- and dust-mixtures, some lighting the dust more easily than the gas, whilst others show a tendency to do the reverse. At Frameries up to 1905 the permitted list consisted of explosives that could be fired direct without stemming into a mixture of 8 per cent of pit-gas (containing 70 per cent of methane) and 92 per cent of air, but about that period the extra test was added of also firing direct into coal-dust suspended in air, with the extra proviso that the *charge limite* should be at least equal in strength to a charge of 175 grms. of No. 1 dynamite.

It was then found that of the thirty permitted explosives on the old list, five inflamed the dust mixture with a smaller charge than that needed to ignite the gas, and that this reduction in *charge limite* brought two of them below the strength needed to pass the test.

The three explosives which had their *charge limite* reduced, but were still strong enough to pass the test, were Yonckite No. 10, Minolite Antigrisouteuse, and Ammon Carbonit, whilst by elimination from the old list it seems probable that Densite III. and Wallonite III. were the two that had their *charge limite* so reduced as to fall below the necessary standard of strength.

The reduction of the gas *charge limite* when the same explosives came to be fired into dust was:—

	Charge limite.		Reduction.
	In gas.	In dust.	
	Grms.	Grms.	Grms.
Yonckite No. 10	800	500	300
Minolite antigrisouteuse	650	400	250
Ammon carbonit	400	300	100

* A Paper read before the Royal Society of Arts, April 2, 1913.

On calculating out the ratio of combustible to oxygen set free for all the explosives in the Belgian permitted list, these three are the only ones that evolve over 15 grms. of surplus oxygen from the explosion of 100 grms., whilst calculation shows that Wallonite III. and Densite III. yield over 20 grms.

We have seen that the 15·5 grms. of free oxygen liberated by Yonckite No. 10 for every 100 grms. used reduces the *charge limite* by 300 grms., so that with over 20 grms. liberated there should be an even greater reduction, which makes the *charge limite* for dust so low that it does not give the necessary strength to pass the test, hence Wallonite III. and Densite III. disappeared from the permitted list.

In a paper by Dr. John Harger, read before the Institution of Mining Engineers in 1912, he showed that the ignition of a mixture of coal-dust and air depended upon the percentage of oxygen in the air, and that, in fact, various kinds of coal-dust had their *charge limite* of oxygen, and that the presence of carbon dioxide rendered the dust still less sensitive.

It is quite clear from this that the liberation of considerable quantities of oxygen by the explosive must make the dust more sensitive, and this is probably the chief reason why the *charge limite* of such explosives is reduced when fired into coal-dust. As far as I have been able to trace this action, it is only when the explosive liberates more than 15 grms. of uncombined oxygen per 100 grms. fired that the *charge limite* is affected, and there are explosives on the Belgian list which give 8, 10, or even 12 grms. per 100 grms. fired, and yet have the same *charge limite* in both gas and dust, and the reason of this is that with these lower quantities the percentage of oxygen in the products of combustion is well below the percentage present in the air, so that the products render the dust less sensitive in the test rather than more.

I think this is where one of the real practical dangers of the new procedure is to be found; if any explosive contains an excess of oxidising material, unless it yields over 17·5 per cent of free oxygen in the products of combustion, it would not show any effect in the test, but in practice it would combine with the coal, and there would always be the danger of sparks or even ignition of the coal.

It must also be borne in mind that coal is frequently fissured, and that where a bore-hole passes through a fissure filled with fire-damp it has on some occasions caused explosion, but in most cases the fissure contains pit-gas in quantity above the explosive limit and nothing happens; if, however, an explosive gives free oxygen, this would attack the pit-gas more readily than the solid coal, and fire might spread down the fissure with disastrous results.

The excess of oxygen yielded by an explosive cannot be determined by explosion in the bomb and analysis of the residual gas, as the free oxygen expends itself on the products from the detonator, fuse, and the cartridge-case.

I am quite aware that explosives giving a large excess of free oxygen have been in use for a considerable time, and that, as far as I know, accidents have not been traced to them; but it must be remembered that one great difference between the Belgian practice and ours is that no shots in the coal itself are allowed except by special permission, which is difficult to obtain, and I submit that the use of explosives giving excess of oxygen in the coal must give rise to a grave and unnecessary danger.

Twenty years ago, in a course of Cantor Lectures before the Royal Society of Arts, I pointed out the danger of large volumes of an easily ignited combustible gas like carbon monoxide being generated by explosives intended for mining work, not only because of the poisonous properties of the gas, but also because a very small percentage of it rendered air containing coal-dust far more explosive than when no gas was present, so that two shots fired in rapid succession might lead to disaster.

At the present time, however, the use of nitroglycerin in a safety explosive to the extent of more than 3 or 4 per cent (a quantity used in some explosives containing large

amounts of ammonium nitrate to ensure complete detonation) can be accomplished safely only by the admixture of carbonaceous materials, such as wood meal and various kinds of flour, to cool the explosion by forming carbon monoxide instead of the dioxide.

The temperature of explosion of blasting gelatin, in which all the carbon is burnt to carbon dioxide, is (according to Bichel) 3216° C.; but if the nitroglycerin is reduced to 25 per cent and is mixed with 40 per cent of wood meal and other bodies, the temperature of explosion is brought down to about one-half, and the products of combustion contain 20 per cent by weight of carbon monoxide, and if a 10-grm. cartridge be fired in a vacuous bomb, the products of combustion contain so much carbon monoxide that they can be lighted at the tap of the bomb and burn with a blue flame.

The larger amount of dilution of the original explosives of this class needed to pass the Rotherham test will increase rather than decrease the volume of carbon monoxide given by the watered down explosive, and this accentuates the danger in another way.

When the products of combustion contain a large enough percentage of carbon monoxide to burn, it is the products as well as the test mixture that contain the combustible gas, and as it is already heated up far above its ignition point, it needs only instantaneous contact with air to produce flame; there is no period of delayed combustion to allow cooling to give safety, and for this reason, as well as on account of its poisonous nature, explosives yielding large percentages of carbon monoxide should be looked upon with grave suspicion, and official tests which practically demand explosives that give either an excess of oxygen or of carbon monoxide are manifestly wrong.

The action of the products formed during explosion upon the coal surface is a most important point, which should be taken into consideration in judging the safety of an explosive. We know that with a properly proportioned explosive yielding nothing but fully oxidised products of combustion, traces of carbon monoxide are always found in the air after the explosive has been fired in a bore-hole in coal, showing that carbon dioxide and water vapour have acted upon the coal surface and have been reduced. These actions are endothermic and use up a large amount of heat, giving increased safety to the explosive. If, however, carbon monoxide instead of dioxide is formed, although the initial explosion is cooler, no subsequent absorption of heat takes place, whilst if free oxygen is generated, a strong exothermic action is set up with the coal, the only saving factor being that it is always accompanied in the products by carbon dioxide and water vapour, which act in the opposite direction.

The only true test of the safety of mining explosives is the practical one of use in coal-mines over many years, and when an explosive has been in use on a large scale for over twenty years, tons of the material having been used and millions of shots fired under every condition conceivable in practice, without a single accident being traceable to its legitimate use, such an explosive holds a certificate of safety that no series of tests under empirical and artificial conditions could ever give it.

In the English permitted list several such will be found, satisfactory in strength and with a character unsmirched by a single ignition of gas or dust in the mine under proper conditions of use; but with the alteration from the procedure in testing for the permitted list adopted at Woolwich to the new conditions existing at Rotherham these will of necessity disappear from the list, and their places be taken by weaker explosives, so that the mine-owner, saddled by the Act of 1912 with the purchase of all explosives used in his mine, will find that the cost in explosives of doing the same amount of work as heretofore will be practically doubled.

By the mere chance of having the Woolwich gallery at work at the time that the Continental methods were introduced, and not being willing to face the expense of a new installation, the Government has acquired seventeen years' experience of practical results under mine conditions, and it appears to me absolutely wrong to cast this aside and to follow different methods, simply because other countries have chosen to adopt them, unless statistics have shown that, per million tons of coal won, our mining explosives have given rise to greater loss of life than those used abroad.

There is another point of view also that may have been overlooked, but which I think is worthy of consideration, and that is that in the Woolwich tests the explosives were simply classified as safe enough to use or not safe enough — no official responsibility was taken in prescribing a quantity that was safe, and I fear that under the new regulations the mine-manager will consider—and not unreasonably—that when a maximum charge of, say, 24 ozs. has been given for an explosive, all responsibility is off his shoulders as long as the 24 oz. limit is not exceeded. As I have shown, I hope, the practical conditions of use are so widely different from the empirical tests we are putting the explosives through, that the personal factor of care in use becomes of enormous value, and I am convinced that a reliable and careful shot-firer blessed with common sense is a greater protection than any tests, rules, and regulations that can be framed, and for that reason view with suspicion anything tending to lessen personal responsibility.

Already the authorities have decided very wisely to extend the time over which the old explosives may be used to December 31st, and I venture to urge strongly that during the next nine months the points raised with regard to the new procedure be considered.

THE LATEST ACHIEVEMENTS AND PROBLEMS OF THE CHEMICAL INDUSTRY.*

By CARL DUISBERG.

(Continued from p. 196).

Materials for Apparatus.

As regards materials for chemical apparatus several new wares must be referred to :—

Quartz.—Apart from the fact that the saltpetre industry of Norway taught us how to absorb dilute nitrous gases in towers 20 metres high, made of granite, a substance which was rarely used for chemical purposes, we have to-day at our disposal tubes, dishes, and vessels of fused quartz, which are stable against acids and heat, and which are manufactured in the same sizes and dimensions as the well-known earthenware vessels.

Refined Steel.—The greatest progress, however, has been made in the manufacture of iron alloys or refined steel.

Thanks to the kindness of Friedrich Krupp, of Essen, I am in the fortunate position to describe a large number of hitherto unknown substances of great importance, of which I exhibit magnificent specimens, photographs, and lantern slides. Just here, however, I must ask you to make one of the landings from the upper air and permit me to deal with the subject at greater length. You will be astonished at the immense progress which has been made to the general benefit of our industry.

Of the greatest interest are the alloys of iron with other heavy metals and metalloids, *i.e.*, alloyed steel.

Instead of carbon, other elements are employed, which likewise enhance the hardness of steel, but prevent the formation of a crystalline micro-structure liable to cracks and flaws. The most important of these elements is nickel.

Nickel Steel.—The readiness with which nickel forms an alloy with iron has long been common knowledge. Even in Bessemer's days, attempts were made in Great Britain to turn out cannons made of steel containing 2 per

* From the *Journal of Industrial and Engineering Chemistry*, iv., No. 10.

cent nickel. The experiments were not successful because the nickel obtained at that time contained impurities, such as copper, arsenic, and sulphur, so that the steel could not be forged. Thirty years later pure nickel, as we know it to-day, made successful results possible. The same was the case with chromium, silicon, and manganese, and not until these elements were produced pure, could successful alloys be manufactured with them, either alone or together with nickel. The chief aim in the manufacture of these alloys is the formation of an amorphous pliable structure of the steel. This result is attained not only by removing more or less carbon, but above all by a certain thermic treatment, namely, by suddenly cooling steel heated to a high temperature, heating again and keeping it at a certain lower temperature. Here you can see two samples of steel; in the one case, the coarse crystallisation of the pure carbon steel before it is forged, and in the other, the same steel refined by the thermic treatment. The difference in the micro-structure of the forged carbon steel and that of the forged and thermically treated nickel steel must also be noted. While carbon steel after forging steel shows a crystalline structure with visible cleavage planes of the crystals, the section of nickel steel displays an amorphous structure closely resembling that of welded iron. For comparison sake, a sample of a welded iron fracture is exhibited. It must not be overlooked, however, that nickel and chrome-nickel steels are twice or three times as hard as welded iron. There are also exhibited test pieces of alloyed steel construction parts to be used in the automobile industry. Notwithstanding the high tensile strength of about 90 kilos. per square millimetre (*i.e.*, about 55 tons per square inch), no fracture is noticeable although they are greatly bent.

Aside from these improvements, which are of such great moment for structural steel, the iron alloys have found many new applications.

I merely mention the different nickel alloys for shipbuilding, electric appliances, and for valves. These valuable alloys containing 23 per cent and more nickel, are non-magnetic, and not affected by atmospheric influences; those containing 30 per cent nickel possess great resistance to electricity, while the coefficient of expansion of steel with 45 per cent nickel is only one-twentieth of that of ordinary steel and not greater than that of glass.

Chromium, Tungsten, and Molybdenum Steel.—It is a very interesting and novel fact that by the thermic treatment alone the micro-structure of the cheaper kinds of unalloyed iron plates and iron shapes is so changed that it becomes three times as resistant to the destructive effect of acids. If alloys of iron with chromium, tungsten, molybdenum, and aluminium in certain proportions are thermically treated, this resistance is increased five-fold, as is shown by samples of ordinary carbon steel and chrome-nickel steel which underwent a treatment with dilute sulphuric acid for fifty-six days.

An alloy of ordinary iron with 5 per cent nickel is an excellent material for withstanding hot caustic soda. Most astonishing properties are displayed by steel alloys containing more than 10 per cent of chromium and a small addition (2—5 per cent) of molybdenum. Such alloys are manufactured in the form of malleable, cast, and forged iron pieces by Krupp according to the patents of Borchers and Monnartz in Aix-la-Chapelle, and in the form of rolled tubes by the Mannesmann Röhrenwerken in Remscheid. These alloys are insoluble not only in dilute hydrochloric acid and sulphuric acid, but also in dilute nitric acid, even with the addition of alkali chlorides, and if they contain about 60 per cent chromium, 35 per cent iron, and 2—3 per cent molybdenum they withstand even boiling aqua regia. You see here samples of this extraordinary steel, after treatment with acids, compared with ordinary steel and cast-iron.

Tool Steel.—It must be especially mentioned that the alloys of iron with chromium, tungsten, and molybdenum tempered by a special process invented by two Americans, Taylor and White, find most important uses as quick turning steel for all kinds of tools.

Vanadium Steel.—The most recent improvements in the manufacture of steel for tools, which must of necessity keep pace in hardness with structural steel, have been made by the employment of vanadium. Unfortunately, this metal, whose use is steadily increasing, is still very dear, and the chemists' problem is to produce it more cheaply. If the price could be reduced perceptibly, metallurgists prophesy a great future for this metal, which exercises a very favourable influence on the micro-structure of steel.

Of great importance are those alloys of iron with chromium, tungsten, and vanadium which possess a high degree of hardness even at 400—500° C. They are needed by engineers for the construction of steam turbines and for the embossing and spraying of metal objects heated to redness, a process which has lately found extensive application. Chemists use these kinds of steel whenever chemical reactions are carried out at high temperatures and pressure, *e.g.*, for the synthesis of ammonia according to Haber's process.

The very latest alloy has now been patented, and is being manufactured by Krupp for the construction of safety vaults and safes. This steel can neither be drilled nor exploded, nor can it be cut by the oxy-hydrogen flame.

Two samples of steel are exhibited, one of ordinary steel in which great holes have been cut in five and a-half minutes by using an oxy-hydrogen flame and in six minutes by an oxy-acetylene burner, and a specimen of this new alloy which has remained intact after being treated with the same oxy-hydrogen and oxy-acetylene flames for one and a-half hours. Let us hope that on this hard and infusible material the scientific safe-burglar will exercise his noble art in vain.

Manganese Steel.—Of the alloys made with manganese, the manganese steel or hard steel, first produced by Robert Hadfield, because of its great wearing qualities, is chiefly used for cast-iron parts of disintegrators and rails of electric tramways. On account of its hardness, this steel is not malleable, but it can be bent in the cold state and is thus very safe against breaking. It is therefore of much interest to the chemical industry where, in almost all branches, grinding operations are carried out.

Silicon Steel.—Finally, I wish to refer to alloys of iron and silicon which contain 1·5—2·5 per cent silicon and a high percentage of carbon. This steel is excellently adapted for tools and springs which must stand high strain. Since steel alloys containing much silicon, although brittle and porous, have proved very stable against acids, they are now being used more and more where such a property is of importance.

Alloys with about 4 per cent silicon, but very poor in carbon, are of greater value than the above. Robert Hadfield first pointed out the importance of this alloy, while Krupp, working in connection with Capito and Klein, a firm of fine-plate rollers in the Rhineland, considerably improved it and introduced it for electric purposes. It is employed in large quantities in the form of sheets of 0·35 mm. (one-seventieth of an inch) thickness for the construction of dynamos, alternate-current motors, and transformers. In Germany alone, the consumption of this alloy already amounts to 8000 tons a year. This material has a resistance to electricity four or five times greater than that of ordinary iron, and loses only half as many watts, so that the injurious Foucault currents are reduced to a minimum. The manufacture of transformers has therefore become much cheaper, for the proportion between iron and copper is much more economical. The production of this silicon iron alloy with its very low percentage of carbon, and that of the chrome-nickel steels almost free from carbon, became possible only after silicon and chromium, entirely free from carbon, could be manufactured by electric smelting processes.

Electro-steel.—Since the electric smelting furnace has

come into use in the steel industry, the problem of removing sulphur, which engaged the attention of chemists for so many years, has been solved. It has been found that the electric furnace process produces a slag free from metal, and such a slag is the prime requisite for the complete desulphuring of the steel bath.

Electrolytic Iron.—Superior to the silicon steel, poor in carbon, in its electric properties the "Ideal" metal for electromagnets is the pure electrolytic iron—first produced by Franz Fischer, of Charlottenburg, and now manufactured by the firm Langbein-Pfanhauser and Co., Leipzig. Formerly it was impossible to produce it free from hydrogen, consequently it was hard and brittle and was not malleable. Only by electrolysing at 100—120° C. and employing an iron salt solution mixed with hygroscopic salts, such as calcium chloride, the iron became free from hydrogen. Its hardness then sinks far below that of silver and gold, and is not much greater than that of aluminium. It possesses the valuable property of becoming magnetic more quickly than ordinary iron containing carbon or silicon, and also of again losing its magnetism more readily, thus considerably increasing the efficiency of electro-motors for which it is used. Among the exhibits, you will find several objects made of this electrolytic iron; for example, a cathode made from an electrolytic iron plate during five days of uninterrupted operation; also plates made by rolling; further, a motor which, if constructed of silicon iron, would furnish 0·5 h.p., but being composed of electrolytic iron, though in use for several months without appreciable signs of wear, it now furnishes 1·3 h.p.; in other words, it is two and a half times as efficient (see *Zeit. Electrochem.*, No. 16, 1909).

With all these new materials at our disposal, among which I must also mention copper, with 10 per cent silicon, and copper nickel, we shall surely be able to improve all sorts of chemical apparatus that suffer so much from wear and tear.

After this short invasion of the domain of metallurgy, we shall now turn our attention to the chemical industry proper, first dealing with the manufacture of the heavy inorganic chemicals.

(To be continued).

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, April 17th, 1913.

Sir ARCHIBALD GEIKIE, K.C.B., President, in the Chair.

PAPERS were read as follows:—

"*Luminosity Curves of Persons having Normal and Abnormal Colour Vision.*" By Dr. W. WATSON, F.R.S.

The author has calculated the form of the luminosity curves corresponding to different degrees of deficiency of the red and green sensation, and shows that in the great majority of cases of colour blindness the observed points agree with the calculated curves, and hence the correctness of Sir W. Abney's sensation curves and his theory as to partial colour blindness is supported. The cases of abnormal luminosity curves given by persons having normal colour vision are shown to be probably due to variation in macular pigmentation.

"*Reflection of X-rays by Crystals.*" By Prof. W. H. BRAGG, F.R.S., and W. L. BRAGG, B.A.

The paper deals with the reflection of a beam of X-rays by the cleavage faces of various crystals, an ionisation method being employed to measure the strength of the reflected rays. The apparatus corresponds to a spectrometer, the parallel planes in which the atoms of the crystal are arranged taking the place of the lines of a grating, and the ionisation chamber that of a telescope. A fine slit in front of the X-ray bulb allows a beam of rays to fall on the face of the crystal, and both crystal and ionisation chamber turn about the axis of the instrument and can be set at any desired angles.

By this method evidence has been found of the existence of three very homogeneous components in the rays from the bulb employed, which are only reflected from the crystal at definite angles. They show as a very strong reflection superimposed on the general reflection which takes place at all angles. Each of these has a definite absorption coefficient in aluminium, and can be recognised when reflected from many crystals.

The angle at which any one of these components is reflected varies for different crystals and different faces of the same crystal, but always in accordance with the formula $n\lambda = 2d \sin\theta$, where d is the spacing of the crystal planes, θ the angle of reflection, n a small integer (1, 2, and 3) and λ a wave-length to be assigned to each component.

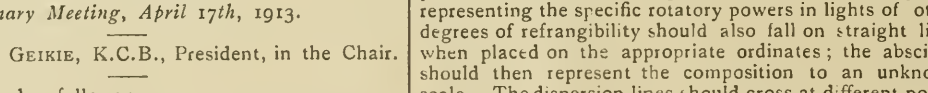
The absorption of the homogeneous rays in different metals corresponds in all respects to the absorption of characteristic X-rays.

"*Fluorescence Spectrum of Iodine Vapour.*" By Prof. J. C. MCLENNAN.

"*Relation between the Crystal-symmetry of the Simpler Organic Compounds and their Molecular Constitution.*" Part I. By W. WAHL, Ph.D.

"*Studies of the Processes Operative in Solutions.* XXVIII. *The Causes of Variation in the Optical Rotatory Power of Organic Compounds and of Anomalous Rotatory Dispersive Power.*" By Prof. H. E. ARMSTRONG, F.R.S., and E. E. WALKER, B.Sc.

Attention is directed to the explanation of the anomalous rotatory dispersive power displayed by some organic compounds, notably, the tartrates, which was given by Biot, the original discoverer of optical rotatory power, viz., that it may be due to the presence of two compounds of opposite rotatory power (+ and −) differing in rotatory dispersive power. This explanation appears to have been generally overlooked. The behaviour to be expected of compounds varying in their optical properties in different ways is discussed. A method is then described of drawing *characteristic* rotatory-dispersion-composition diagrams from observations made with solutions differing in concentration, in temperature, or in the nature of the solvent, the assumption being made that the composition of the supposed mixture studied is a linear function of the specific rotatory power in each coloured light, in which case all the points representing the specific rotatory powers in lights of other degrees of refrangibility should also fall on straight lines when placed on the appropriate ordinates; the abscissæ should then represent the composition to an unknown scale. The dispersion lines should cross at different points in the case of mixtures of anomalous dispersive power. This is shown to be true of methylic and ethylic tartrates and of the orthonitrobenzoyltetrahydroquinaldine described recently by Pope and Winmill. It is therefore argued that in these and similar cases the anomalous dispersive power that is noticeable is due to the presence in the solution of isodynamic forms of the "substance" studied—forms so different in structure that their rotatory powers are of opposite sign and that their dispersive powers vary at different rates; in the case of the tartrates, for example, of the two forms—



The results arrived at serve to explain the apparently abnormal variation in optical behaviour often noticed in optically active compounds; they also appear to be of significance as indicating a relation among solvents generally, and underlying their action towards substances generally of a very definite and regular character; each solvent would seem to have its definite sphere and mode

of action, so that any two solvents behave relatively always in the same way towards solutes generally, apart from the exceptional cases in which some special property or the solute comes into operation to disturb regularity of action.

CHEMICAL SOCIETY.

Ordinary Meeting, April 3rd, 1913.

Prof. W. H. PERKIN, LL.D., F.R.S., President, in the Chair.

THE PRESIDENT referred to the loss sustained by the Society through death on March 29, 1913, of Mr. John Heron, who was elected a Fellow on June 15, 1876.

Messrs. Percy C. Burr, J. A. Christie, and E. A. Buckle were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. John Percy Batey, M.Sc.Tech., 3, Minorca Road, Weybridge; George Frederick William Blackburn, 25, Rowington Road, Norwich; Arthur Hawker Cox, 4, St. Peter's Place, Brighton; Arthur Ernest Crutchley, 230, Albert Road, Handsworth, Birmingham; Vasanji Premji Dalal, M.A., B.Sc., "Gujana Geha," Central Hindu College, Benares; Percy Hutchinson, B.Sc., 74, Hotham Road, Putney, S.W.; Joseph Stuart Lawson, 18, Old Swan Lane, E.C.; Harold Charles Lloyd, B.Sc., Ferndale, Trinity Square, Llandudno; John Robert Ruffley, 130, Worsley Road, Farnworth, Lancs.; Herbert Sutcliffe Sarrewsbury, Government Laboratory, Trinidad, B.W.I; Panks James Wigginton, 54, Grand Parade, Brighton; William John Young, M.Sc., D.Sc., Australian Institute of Tropical Medicine, Townsville, N. Queensland.

Of the following papers, those marked * were read:—

*77. "*Studies in the Camphane Series.* Part XXXIV. *Configuration of the Eight Oximino-derivatives of Camphorquinone.*" By MARTIN ONSLOW FORSTER.

Based on the recognition of stable *iso*nitrosocamphor as the *syn*-modification (*Trans.*, 1905, lxxxvii., 232) the properties of the two forms of *iso*nitrosoepicamphor and of the four camphorquinonedioximes have been reviewed in such a way as to suggest the configuration of the eight oximino-derivatives of camphorquinone. The scheme thus elaborated agrees in every detail with the experimental relationship between the four monoximes and the four dioximes.

*78. "*The Action of Ozone on Cellulose.* Part III. *Action on Beech Wood (Lignocellulose).*" By CHARLES DORÉE and MARY CUNNINGHAM.

In continuation of previous work on the simple lignocellulose jute (*Trans.*, 1912, ci., 503) the action of ozone on the more complex tissues of the woods has been examined. In the presence of moisture, ozone rapidly attacks the wood substance, producing carbon dioxide and acidic substances. Results were given showing the production of these per hour from one to twelve hours. As the result of oxidation with ozone a considerable proportion of the wood is converted into derivatives soluble in water; after twelve hours the loss in weight is some 40 per cent. The water-digest contains acetic, formic, and other reducing acids, and yields furfuraldehyde. Vanillin was not detected. The properties of a wood residue obtained after thirty hours' treatment were given in detail. This contained one half of the furfuraldehyde-yielding groups, but only one-third of the methoxyl groupings of the original wood. The results are well explained by the formulation of the lignone complex given by Cross and Bevan ("Researches on Cellulose," iii., 104), but they do not lend support to the coniferyl alcohol formula proposed by Klason.

DISCUSSION.

Mr. C. F. CROSS desired to state that he had followed these investigations, and considered that they established the value of the authors' method as one of progressive constitutional dissection of the lignocellulose. With a general verification of the schematic formula for lignone in "Researches on Cellulose" iii. (Cross and Bevan), the results further weakened the case for the formulæ proposed by Klason and Czapek.

*79. "*The Formation of Cyclic Compounds from Derivatives of 2 : 2'-Ditolyl.*" By JAMES KENNER.

The appearance of a paper by Weinzenböck (*Monatsh.*, 1913, xxxiv., 193) has necessitated publication of results obtained by the author in continuation of previous work (Kenner and Turner, *Trans.*, 1911, xcix., 2101; Kenner, *Proc.*, 1912, xxviii., 187). The results obtained have rendered the more important derivatives of dibenzo*cyclo*heptadiene accessible by the usual reactions.

Thus the *hydrazide* of *dibenzo*cyclo*heptadienecarboxylic acid*, needles, m. p. 176°, has been converted into *dibenzo*cyclo*heptadienylurethane*, small prisms, m. p. 88°, from which the *hydrochloride* of 1 *amino* 3 : 5 *dibenzo*-Δ3 : 5-cyclo*heptadiene*, needles, m. p. 287°, is obtained by hydrolysis with concentrated hydrochloric acid. The amine also results when the oxime of dibenzo*cyclo*heptadienone is reduced in alcoholic solution with sodium, and has been further characterised by its *platinichloride*, a canary-yellow precipitate, m. p. 266°, and its *acetyl* derivative, needles, m. p. 147°. When dibenzo*cyclo*heptadienylamine hydrochloride is distilled, it yields 3 : 5-*dibenzo*-Δ1 : 3 : 5-cyclo*heptatriene*, the *picrate* of which forms copper-coloured needles, m. p. 137°.

Further, *diethyl* 2 : 2'-*ditolyl* ω ω' *dicarboxylate*, rhombic crystals, m. p. 49°, is readily converted in boiling benzene solution under the influence of sodium into *ethyl* 3 : 5-*dibenzo* Δ3 : 5-cyclo*heptadien*-1-*one*-2 *carboxylate*; this compound gives an indigo-blue coloration with ferric chloride, and yields a dirty green *copper* salt, m. p. 253°, when its ethereal solution is shaken with aqueous copper acetate solution.

DISCUSSION.

Mr. JOHN H. CHRISTIE suggested that if the two outside carboxyl groups of the diphenyltetracarboxylic acid were esterified, it might be possible to cause anhydride formation between the two inner carboxyl groups, with formation of a seven carbon ring instead of two five-carbon rings.

Dr. KENNER, in reply, said his calculation of the strain in the dibenzo*cyclo*heptadiene ring had only been carried out on the assumption that all its carbon atoms were coplanar. Experiments, similar to those suggested by the President, had been carried out, and were described in the full communication (compare *Proc.*, 1912, xxviii., 187). The various di-ester acids of diphenyltetracarboxylic acid were receiving attention, but the experiments in this direction were only in their initial stage.

*80. "*The New Oxide of Carbon, Mellitic Anhydride, and Derivatives of Mellitic Acid.*" (Preliminary Note). By WILLIAM JOHN JARRARD.

In view of the preparation of a new oxide of carbon by Hans Meyer and Steiner (*Ber.*, 1913, xlvi., 813) and the statement that the results of further work on mellitic acid will shortly be published, the following preliminary account of the work done by the author on this compound and other derivatives of mellitic acid during the past two years was communicated.

Publication of these results was delayed on account of the somewhat laborious method of preparing the mellitic acid, by the oxidation of carbon by nitric acid and potassium chlorate, precipitation of the barium salt, and fractional crystallisation of the ammonium salt, no commercial source of mellitic acid being then available.

The two anhydrides of mellitic acid have been obtained by methods differing from those used by Hans Meyer and Steiner.

A dianhydride was obtained by dissolving mellitic acid in fuming sulphuric acid (containing 70 per cent of sulphur trioxide), and slowly adding water. The dianhydride is precipitated as a white, amorphous, hygroscopic powder, separating from solutions in ether or acetone in crystals

containing these solvents. The crystals from acetone contain one molecule of acetone of crystallisation, and decompose on keeping. This anhydride gives characteristic colour reactions when heated with nitrobenzene, naphthalene, or phenanthrene.

The trianhydride, $C_{12}O_9$, was prepared by the action of thionyl chloride on carefully dried silver mellitate suspended in ether or benzene (Denham, *Proc.*, 1909, xxv., 294). An intermediate compound is formed, which is decomposed completely with the elimination of sulphur dioxide only after continued boiling. The dianhydride is always produced at the same time, probably owing to the formation of mellitic acid from the silver mellitate by hydrogen chloride, which is retained in thionyl chloride with great persistency. By fractional sublimation of the product of the reaction in a vacuum there may be separated the dianhydride, pyromellitic anhydride, and a substance which gives the same colour reactions with nitrobenzene, naphthalene, and phenanthrene as the oxide prepared by Hans Meyer and Steiner, and which acts as the trianhydride of mellitic acid on titration with baryta solution. The formation of pyromellitic anhydride, which probably results from the decomposition of the dianhydride, confirms the formula suggested by Hans Meyer and Steiner for the latter substance.

Although sufficient of the pure trianhydride for a complete analysis has not yet been obtained, this compound was completely identified by the formation of a *triethyl* ester of mellitic acid (m. p. 165° with decomposition) by the action of ethyl alcohol on the crude substance. Ethyl alcohol does not act very readily on this anhydride, the action being complete only after boiling the mixture for some time. Methyl alcohol, however, reacts much more readily. All the common inorganic salts of this triethyl ester are soluble in water. The *sodium*, *barium*, and *silver* salts have been prepared by precipitation in alcoholic solutions and analysed.

When heated in a vacuum the triethyl ester does not form the trianhydride, as might be expected. It melts at 140°, loses one molecular proportion of ethyl alcohol, and forms the monoanhydride of a diethyl ester of mellitic acid (octahedral crystals from ethyl acetate, m. p. 143—144°). On further heating, one molecular proportion of carbon dioxide is liberated, and an anhydride of a diethyl ester of benzenepentacarboxylic acid results (leaflets softening at 210°, and melting completely at 235°).

Rhead and Wheeler (*Trans.*, 1913, ciii., 461) have recently brought forward evidence that during the combustion of carbon in oxygen, an oxide of carbon is formed, which breaks up into carbon monoxide and carbon dioxide, and suggest that this compound is similar to mellitic acid or its trianhydride.

In this connection it is of interest to note that these gases are obtained when the vapours from mellitic acid or the crude anhydride are passed through a hot tube in an atmosphere of nitrogen free from oxygen.

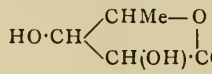
The following derivatives of mellitic acid have been prepared, and are at present under investigation:—The *trimethyl* ester from the trianhydride, the *trimethyl triethyl* ester (prisms, m. p. 65°), the *triamide*, corresponding with the triethyl and trimethyl esters, and *hexa-amide* (a white amorphous powder, m. p. above 300°, which turns bright blue on exposure to light, but loses this colour when placed in darkness).

The ultra-violet absorption spectra of alcoholic solutions of mellitic acid and its hexamethyl and hexaethyl esters have been examined at various dilutions. These solutions exhibit strong general absorption, but no selective absorption.

81. "*Synthesis of a Methyl Tetrose.*" (Preliminary Note). By ROBERT GILMOUR.

In view of the fact that no synthesis of a methyl pentose has been recorded (with the exception of the recent synthesis by Fischer from glucose triacetylbromohydrin, which appeared after the work described in this note had been started), it seemed of some importance to attempt the preparation of such a compound.

The most suitable material from which to start appeared to be the dihydroxyvalerolactone, which had been prepared by Thiele (*Ann.*, 1902, cccxix., 194) by the oxidation of β-angelicalactone with potassium permanganate, and which he considered to possess the structure:—



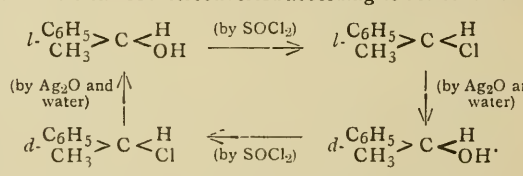
On the analogy of the sugar lactones this substance ought to yield a methyl tetrose on reduction with sodium amalgam. From the product of reduction an osazone was isolated, which proved to be a *methyl tetrosazone*.

The compound forms yellow micro-crystalline needles, very sparingly soluble in water or ether, but readily so in alcohol, and melts at 140–142°. It must be regarded as the osazone of an inactive methyl tetrose.

Unfortunately, the preparation of the dihydroxyvalerolactone in quantity is a laborious and tedious process, and the yield is small. It is proposed, however, to carry the synthesis a stage further, in order to obtain, if possible, a methyl pentose. The resolution of dihydroxyvalerolactone, is also contemplated with a view to the isolation of the sugars in an optically active condition.

82. "*Experiments on the Walden Inversion.* Part IX. *Interconversion of the Optically Active Phenylmethylcarbinols.*" By ALEX. MCKENZIE and GEORGE WILLIAM CLOUGH.

It was shown that the optically active phenylmethylcarbinols can be interconverted according to the scheme:—



83. "*Externally Compensated Hydroxyhydrazinohydrindene, its Derivatives and Resolution into Optically Active Components.*" By DAVID HENRY PEACOCK.

The author has prepared *1-hydroxy-2-hydrazinohydrindene*, $C_6H_4<^{CH(OH)}_{CH_2}>CH\cdot NH\cdot NH_2$, by the action of hydrazine hydrate on bromohydroxyhydrindene, and has resolved it into optically active components with the aid of *d*-tartaric acid. Several salts and derivatives of the externally compensated and optically active hydrazine were described.

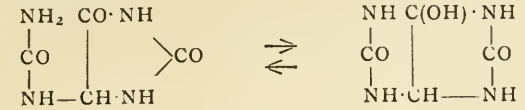
84. "*Studies in Substituted Quaternary Azonium Compounds containing an Asymmetric Nitrogen Atom.* Part I. *Resolution of Phenylmethylethylazonium Iodide into Optically Active Components.*" By BAWA KARTAR SINGH.

The author has prepared externally compensated *phenylmethylethylazonium iodide*, $(C_6H_5)(C_2H_5)(CH_3)(NH_2)NI$, and has obtained salts of the corresponding lævorotatory azonium compound with the aid of *d*-camphor-β-sulphonic, *d*-tartaric, and *d*-camphoric acids. The *l*-azonium radicle contained in the compounds described readily undergoes racemisation.

85. "*The Constitution of Allantoin.*" By ARTHUR WALSH TITHERLEY.

Allantoin, in spite of the accepted unsymmetrical Formula I., proposed by Grimaux, functions as a symmetrical compound in regard to its alkyl derivatives, and only two methyl derivatives (α and β) appear to be capable of existence. Further, Mendel and Dakin (*Journ. Biol. Chem.*, 1910, vii., 153) pointed out that, in spite of the asymmetric carbon atom in Formula I., allantoin cannot be obtained in an optically active form. The author reconciles these and other contradictory features of allantoin with Grimaux's formula by supposing tauto-

merism, producing the symmetrical ring form (II.), to come into play :—



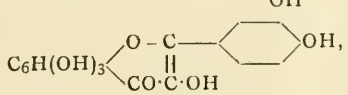
I. II.

Such tautomerism involving the wandering of an amidic or hydroxylic hydrogen atom in such a way as to produce either an open-chain or ring system, is analogous to the "metoxazone tautomerism" observed by the author among acyl derivatives of salicylamide. All the facts relating to allantoin and its derivatives appear to be in harmony, with the supposition that Formula II. represents the pseudo-form of allantoin and Formula I. its normal constitution.

86. "*Gossypetin.*" By Arthur George Perkin.

Gossypetin, $C_{15}H_{10}O_8$ (*Trans.*, 1899, lxxv., 826; 1909, cxv., 1855, 2181), exists as glucoside in the ordinary Indian cotton flower, *Gossypium herbaceum*, in conjunction with quercetin. *Gossypetin hexamethyl ether*, $C_{15}H_4O_2(OMe)_6$, colourless needles, m. p. 170—172°, can be prepared by means of methyl iodide, and when hydrolysed with alcoholic potassium hydroxide gives protocatechuic acid dimethyl ether and *gossypitol tetramethyl ether*, $C_{12}H_{16}O_6$, needles, m. p. 115—116°. *Gossypetin hexaethyl ether*, $C_{15}H_4O_2(OEt)_6$, m. p. 144—146°, in a similar manner gives protocatechuic acid dietnyl ether and *gossypitol tetraethyl ether*, $C_{16}H_{24}O_6$, m. p. 110—111°. The latter yields the oxime, $C_{16}H_{25}O_6N$, m. p. 127—129°, with permanganate an acid, $C_{14}H_{18}O_7$, m. p. 154—155°, probably *hydroxytriethoxybenzeneglyoxylic acid*, and there is little doubt that it possesses the constitution $HO{\cdot}C_6H(OEt)_3{\cdot}CO{\cdot}CH_2{\cdot}OEt$.

With alcoholic *p*-benzoquinone, or by alkaline oxidation, gossypetin gives *gossypitone*, $C_{15}H_8O_8$, dull red microscopic needles, soluble in dilute alkali with a blue colour, and this reaction also occurs during the dyeing operation when mordanted wool is employed. Gossypitone is a quinone, and with sulphurous acid is re-converted into gossypetin, but is not identical with the quercetone described by Nierenstein and Wheldale (*Ber.*, 1911, xliv., 3487). Whether gossypitone is to be regarded is an "anthocyanin" (compare Wheldale, *Proc. Roy. Soc.*, 1909, B, lxxxi., 44), and indirectly responsible for the red of the cotton petal (such as that of *G. arboreum*), is considered uncertain, although a reddish violet, crystalline compound can be obtained from the gossypetin glucoside. To gossypetin the constitution of an hexahydroxyflavone isomeric with myricetin and quercetagetin (*Trans.*, 1913, ciii., 212) is assigned—



but as in the case of the latter colouring matter the position of the hydroxyls in the tetrahydroxybenzene nucleus remains undecided.

87. "*The Alleged Permeability of Glass to Halogen Vapours.*" By James Brierley Firth.

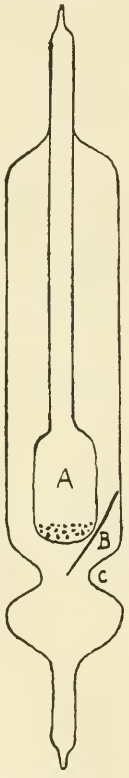
Landolt (*Zeit. Phys. Chem.*, 1906, lv., 589), in his experiments on the conservation of weight in chemical reactions, always obtained a slight loss. He concludes that this loss may be due to the escape of vapours through the walls of the containing vessel.

In later experiments (*Sitzungsber. K. Akad. Berlin*, 1908, 354) he shows that the loss may be due to the development of heat, causing a change in the amount of water condensed on the sides of the vessels, and also a slight change in volume of the vessel due to change of temperature and pressure. After making these allowances, Landolt concludes that there is no loss of weight during chemical reaction.

Zengelis (*Zeit. Phys. Chem.*, 1909, lxv., 341) describes experiments, from which he concludes that various vapours can readily pass through glass. He took a series of air-tight flasks, sealed with paraffin, containing respectively chlorine, bromine, and iodine; on the outside of these flasks a piece of silver foil was fixed, and then enclosed in separate air-tight vessels. The silver was found to be distinctly attacked after the following periods :—(*a*) Chlorine, fifty days; (*b*) bromine, fifty days; (*c*) iodine, three days.

The effect was more rapid when the outer vessel was exhausted.

Zengelis concludes that in Landolt's experiments there is always a real loss of weight, and explains the loss as being due to the escape of the various vapours through the walls of the containing vessel.



Stock and Heyneman (*Ber.*, 1909, xlii., 1800) were unable, in the case of iodine, to confirm Zengelis's results even after three months.

Zengelis (*Zeit. Phys. Chem.*, 1910, lxxii., 425) repeated his experiments, and endeavoured to determine the loss in weight, but his results were irregular.

The author has endeavoured to repeat Zengelis's experiments with a somewhat modified form of apparatus (see Fig.). It consists essentially of a thin bulb, A, which contains the halogen, and an outer jacket, which contains a piece of bright clean silver foil, B, held in position by constriction, C. The whole apparatus was made from ordinary soft glass tubing.

The conditions of experiment were varied as follows :—(1) Outer and inner tubes full of air at atmospheric pressure, and at the room temperature; (2) outer tube vacuous, the inner tube as in 1; (3) inner tube vacuous, the outer tube as in 1; (4) outer and inner tubes vacuous.

Bulb A contained in one series a small quantity of pure iodine, and in a second series pure bromine. A number of pieces of apparatus, as described above, were made, and allowed to remain at room temperature. They were carefully examined periodically, and after a period of two years there was not the slightest indication of the presence of any silver haloid on the surface of the silver.

Another series of experiments was made, in which the tubes were heated for a period of fifty days at 360°, and then allowed to remain for two years, and in this case also no halogen had penetrated the glass.

The above experiments show that ordinary glass is not permeable to the vapours of iodine and bromine at 360° after fifty days, and after two years at the ordinary temperature.

(We are indebted to the Chemical Society for permission to use this woodcut).

88. "*Preparation of Amine Nitrites.*" By Panchanan Neogi.

In continuation of the author's work on the isolation of ammonium nitrite (Neogi and Adhicory, *Trans.*, 1911, xcix., 116) and coniinium nitrite (Neogi, *Trans.*, 1912, ci., 1608) from mixtures of the hydrochlorides of the bases and sodium or potassium nitrite, the following nitrites have been prepared in a similar manner :—Benzylammonium nitrite, methylammonium nitrite, ethylammonium nitrite, dimethylammonium nitrite, piperidinium nitrite, diethylammonium nitrite, trimethylammonium nitrite, triethyl-

ammonium nitrite. The general method of preparation consists in steam distillation in a vacuum. In the case of those nitrites, however, which sublime in a vacuum when heated, they have been prepared by vacuum sublimation also. The actual isolation of these amine nitrites from mixtures of their hydrochlorides and alkali nitrites amply confirms the theory advanced by the author (*Proc.*, 1911, xxvii., 242; *Trans.*, 1912, ci., 1610) that an amine nitrite is an intermediate compound in the well known reaction between nitrous acid and the primary, secondary, and tertiary amines, the purely aromatic amines being excepted.

89. "*A Criticism of some Recent Viscosity Investigations.*" By EUGENE C. BINGHAM.

The use of viscometers of the Ostwald type for measuring the viscosity of liquids where the viscosities extend over a considerable range of values has led observers to unsatisfactory results. The reason is that in this form of apparatus the pressure is not variable at will, and therefore the neglected kinetic energy correction becomes very large with very fluid substances; with more viscous substances the time of flow is inconveniently great, and as a result of the sluggish flow, the danger of partial clogging of the capillary becomes imminent. The prevalent idea that a kinetic energy correction is not applicable to viscometers of the Ostwald type is erroneous.

In interpreting the results of viscosity measurements, the old assumption is still being made without supporting evidence that the viscosities of homogeneous mixtures of liquids are additive. Since this omission is made in the face of abundant evidence that fluidities—and therefore necessarily not viscosities—are additive, the subsequent reasoning loses its cogency.

90. "*Cyanogen and Cyanogen Bromide.*" By AUGUSTUS EDWARD DIXON and JOHN TAYLOR.

Although cyanogen bromide is not ionised by water, its aqueous solution reacts with a number of ionised substances. In most cases (if not in all) the primary change is due to combination of the cyanogen with the more electro-positive ion, the bromine taking the less electro-positive; secondary action, however, may occur amongst the products. These phenomena may be explained by the supposition that additive compounds are first produced by union of the ions M and X, with the unsaturated carbon atom, the less electropositive, X, taking up the *syn*-position with respect to the bromine, thus,—

$$\begin{matrix} C \\ \| \\ N\cdot Br \end{matrix} + MX = \begin{matrix} M\cdot C\cdot X \\ \| \\ N\cdot Br \end{matrix};$$

whereupon, decomposition follows, into $M\cdot CN + X\cdot Br$. The latter may now act on the cyanide, or other attackable material present (including sometimes MX itself), or may decompose; for example, with alkali hydroxide, cyanide and hypobromite are formed; these react, yielding cyanate and bromide; but if carbamide is present the hypobromite attacks it, and nitrogen escapes.

With hydrogen sulphide, if much free hydrochloric acid is present, the products are hydrogen cyanide, hydrobromic acid, and sulphur:—

$$\begin{matrix} H\cdot C\cdot SH \\ \| \\ N\cdot Br \end{matrix} \rightarrow HCN + HSBr \rightarrow HCN + HBr + S.$$

In the absence of free acid, much thiocyanic acid is formed, probably through the change $HCN + HSBr = HSCN + HBr$. With sodium thiosulphate a complex reaction occurs, which is thus explained:—

$$\begin{matrix} NaO\cdot SO_2\cdot S\cdot C\cdot Na \\ \| \\ Br\cdot N \end{matrix} \rightarrow NaCN + NaO\cdot SO_2\cdot SBr$$

and $NaO\cdot SO_2\cdot SBr + NaS\cdot SO_2\cdot ONa = Na_2S_4O_6 + NaBr$. The cyanide now reacts with the tetrathionate, producing sulphite, sulphate, and thiocyanate.

Thiocarbamide and cyanogen bromide in the presence of sodium hydrogen carbonate, yield thiocyanate, bromide, and cyanamide; but in presence of a strong acid give hydrogen cyanide, hydrobromic acid, and a salt of formamidine disulphide.

For cyanogen the authors suggest, as preferable to the formula, $N\vdots C\cdot C\vdots N$, usually adopted, the ring formula

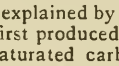
$$\begin{matrix} C = C \\ \| \quad \| \\ N - N \end{matrix}.$$

91. "*The Spectroscopic Investigation of the Carbinol-ammonium Base Isomerism.* Part II. *Derivatives of Cinnamylidene-p-toluidine.*" By CHARLES KENNETH TINKLER.

The action of methyl iodide and of methyl sulphate on cinnamylidene-*p*-toluidine has been investigated with a view to the preparation of a stable quaternary salt of an azomethine base. Additive compounds were obtained, but on crystallisation from alcohol the corresponding hydriodide and methyl hydrogen sulphate were obtained. These additive compounds are decomposed by water, soluble base, or soluble cyanide, and in this respect resemble the methiodide and ethiodide of benzylidene-*p*-toluidine described by Hantzsch and Schwab (*Ber.*, 1901, xxxiv., 837).

The ultra-violet absorption spectra of alcoholic solutions of the quaternary salts of cinnamylidene-*p*-toluidine containing soluble base or cyanide are in agreement with those of the parent base, and are quite distinct from those of α-*p*-toluidino-γ-phenyl*iso*crotononitrile, $CHPh:CH\cdot CH(CN)\cdot NH\cdot C_6H_4Me$, with which they would be in agreement if a ψ-base or cyanide were produced.

The salts of cinnamylidene-*p*-toluidine are much darker in colour than the parent base, and in this respect resemble the hydrochlorides of azomethine bases described by F. G. Pope and Fleming (*Trans.*, 1908, xciii., 1904) and by F. J. Moore and co-workers (*Journ. Am. Chem. Soc.*, 1908, xxx., 394, &c.). These investigators assign a quinonoid constitution to these salts. It will be observed that by assigning such a constitution to cinnamylidene-*p*-toluidine methiodide (I.), the non-formation of a carbinol (II.) from this substance would be readily explained:—

$CHPh:CH\cdot CHMe\cdot N:$  Me, I

I.

$CHPh:CH\cdot CH(OH)\cdot NMe\cdot C_6H_4Me$

II.

Cinnamylidene-p-toluidine (m. p. 83°) was prepared in the usual manner. The *hydrochloride* (m. p. 188—190°), *hydrobromide* (m. p. 206°), *hydriodide* (m. p. 183°), *nitrate*, *hydrogen sulphate* (m. p. 193°), and *methosulphate* (m. p. 205°) were prepared for investigation in connection with Hantzsch's theory of chromoisomerism (*Ber.*, 1911, xliv., 1783).

α-p *Toluidino-γ-phenyl*iso*crotononitrile* (m. p. 119°) was prepared by the condensation of cinnamaldehydecyanohydrin and *p*-toluidine, and also by the action of anhydrous hydrogen cyanide on cinnamylidene-*p*-toluidine.

(To be continued).

FARADAY SOCIETY.

Ordinary Meeting, April 4th, 1913.

Dr. GILBERT J. FOWLER in the Chair.

THE Meeting was held at the Municipal School of Technology, Manchester, conjointly with the Manchester Section of the Society of Chemical Industry, when a General Discussion on "*The Corrosion of Iron and Steel*" took place.

Mr. BERTRAM LAMBERT, M.A. (Oxford) read a paper on "*An Electrolytic Theory of the Corrosion of Iron.*" (See CHEMICAL NEWS, cvii., 184).

Prof. W. W. Haldane Gee, M.Sc.Tech., B.Sc. (Manchester), delivered a Lecture, illustrated by experiments and lantern slides, on "*The Electrolytic Methods for Preventing the Corrosion of Metals.*"

He showed that the corrosion of metals can be lessened or prevented in two ways —(1) By connecting the metal to be protected to a more electro-positive metal, so that a primary cell is produced; (2) by making the metal to be protected the cathode in an electrolytic cell supplied by an external electrical pressure. Various types of primary cell arrangements that could be employed in practice were classified. The efficiency of the cell for protection will depend on the current density at the cathode, and this will be controlled by the resistance of the cell and the effective voltage. The importance of overvoltage in determining the effective voltage was discussed. The history of Sir Humphry Davy's application of zinc and iron protection for the prevention of the corrosion of the copper sheathing of ships and subsequent inventions for the protection of condensers and pipes were detailed. The patents of Harris and Anderson, in which aluminium alloys are used for the prevention of the corrosion of condenser tubes, were shown to be primary cell methods. In the case of the use of zinc in boilers was involved a knowledge of the electrolytic resistance of the boiler waters and the effective voltage at temperatures from 150—200° C., concerning which there is great need of experimental data. The amount of zinc used in some marine boilers is as great as from 400—600 lbs. of rolled zinc per annum. If the zinc is efficient in producing electrical currents then the average current may be from 17 to 25 ampères. It was obvious that such currents would be obtained much more economically by the use of a dynamo. The direct use of electrical currents has been the basis of a number of patents. Those of Mr. Elliott Cumberland were especially described. Iron anodes are placed in the water of the boiler, which latter is made the cathode. A low voltage of supply provided by a small motor-generator is used. The method has proved effective not only in preventing corrosion, but also in removing scale from the heating surface and preventing its formation. Experiments carried out at the Manchester School of Technology have shown that the current densities necessary to protect iron, copper, and other metals from the corrosion of fresh and salt water are of low value, and hence in the cases of boilers and condensers the annual cost of the electrical energy required is a small item. The chief cost will be in the renewal of anodes. Harris and Anderson have also applied electrical currents for the prevention of the corrosion of condensers. They find that a condenser with a cooling surface of 1025 sq. ft. requires only 2 volts and 2 ampères, and the special anodes used by them cost from £3 5s. per 1000 sq. ft. per annum. The use of electrical currents may also be applied in chemical works to prevent the corrosion of metallic screens and vessels from acid liquids.

Mr. J. T. Crabtree, M.Sc., read a paper on "*The Nature of Overvoltage.*"

This may be regarded either as the excess of the anodic or cathodic decomposition voltage of a dilute acid with a given electrode over that for platinised platinum, or as the excess of the back E.M.F. set up as an electrode (anode or cathode) after polarisation over that set up by a platinised platinum plate under identical conditions.

This back E.M.F. was determined by alternately polarising an electrode and measuring its single potential difference by means of a potentiometer, alternate connection between the latter and the primary circuit being made by means of a rotating commutator.

Overvoltage is affected by the time of application and current density of the polarising current, the nature of the electrolyte and electrode employed, and by the thickness of the latter. Since these factors also affect the back E.M.F. of platinum, a comparison electrode was employed consisting of a thin deposit of platinum on Jena glass, the back E.M.F. of which is constant with time.

The overvoltage of a metal was taken as the difference between the back E.M.F. set up after an application of the polarising current for thirty minutes at a given current density, in N/10 acid, and that set up by the above electrode under similar conditions.

It is probable that overvoltage is simply a manifestation of the difference between the rate of production of ions at the electrode and of the combination of these to form complexes. Probably after being discharged the ions pass into a metastable condition and give rise to a back E.M.F. The catalytic activity of the electrode is probably an important factor as affecting this velocity of reaction, and the difference in catalytic activity of various metals under different conditions of texture, temperature, &c., would explain why the overvoltage varies largely with different metals under different conditions.

Overvoltage may be of importance in the case of the corrosion of a metal as either—

(*a*) Having a tendency to retard the deposition of hydrogen or oxygen on its surface, which might tend to assist or prevent corrosion.

(*b*) By setting up a high back E.M.F. which would diminish the effect of a decomposing current in cases of corrosion due to electrolysis.

(*c*) By assisting or preventing the solution of a metal. The condition that a metal may dissolve in an acid and evolve hydrogen is given by the relation —

$$\text{E.M.F. of metal} - \text{back E.M.F. of hydrogen} > \eta\ ;$$

where η = overvoltage of metal. If η is large, no solution of the metal can occur. This is apparent with galvanised iron, where, owing to the overvoltage of the zinc, very little solution of iron takes place, the latter assuming the overvoltage of the external metal.

In view of the absence of any suitable factor to indicate the tendency of a metal to corrode, future experiments may indicate a parallelism between the overvoltage of a metal and its corrosion factor.

Dr. W. Rosenhain, F.R.S., read a paper entitled "*Note on a Specimen of Ancient Iron from Ceylon.*"

The reading of the papers was followed by a long discussion. A number of specimens of corroded metals was exhibited.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Seances de l'Academie des Sciences. Vol. clvi., No. 6, February 10, 1913.

Direct Hydrogenation of Phenylacetic Ethers. Preparation of Cyclohexylacetic Acid.—Paul Sabatier and M. Murat.—The direct method of hydrogenation over nickel of the ethers of phenylacetic acid transforms them quantitatively, without any loss or formation of by-products, into the corresponding ethers of cyclohexylacetic acid, $C_6H_{11}.CH_2.CO_2H$. These ethers are colourless liquids, lighter than water, with an odour which is not disagreeable at first, but clings very persistently and unpleasantly to any objects exposed to it. They are very readily saponified, giving a salt from which the free acid can be liberated by treatment with dilute sulphuric acid. Cyclohexylacetic acid forms white crystals, melting at 32° and of density approximately that of water. It turns litmus red.

Decomposition of Water by α-Rays.—William Duane and Otto Scheuer.—The α-rays decompose water, whatever its state, into hydrogen and oxygen. In the solid state at −183° the product is detonating gas, while

in the liquid state excess of hydrogen is formed, the oxygen combining with some of the water to give hydrogen peroxide. In the gaseous state, also, excess of hydrogen is formed. The quantity of liquid water decomposed is proportional to the intensity of the radiation. In the case of ice and water-vapour if the gas formed is allowed to remain exposed to the action of the rays, re combination occurs.

Catalytic Hydrogenation of Camphorone.—Marcel Godchot and Felix Taboury.—When camphorone is subjected to the action of hydrogen and reduced nickel at 130° it is transformed quantitatively into dihydrocamphorone, boiling at 182—183°. At 280° camphorone and dihydrocamphorone are both converted by nickel and hydrogen into 1-methyl-3-isopropyl-cyclopentane. When organo magnesium compounds act on dihydrocamphorone the two isomeric hydrocarbons are obtained which are derived from it by dehydration, and which, when hydrogenated at 180° over nickel, give the corresponding saturated hydrocarbon.

Case of Dimorphism.—A. Duffour.—When benzoyl vanillic alcohol is obtained by hydrogenating vanilline benzoate by means of hydrogen in presence of platinum black it forms triclinic crystals, while monoclinic crystals of the same chemical compound are obtained when a molecule of benzoyl chloride acts on a molecule of sodium vanillic alcoholate. All attempts to convert the one type of crystals into the other failed, but probably only the triclinic variety is stable, the monoclinic form existing in a state of false equilibrium.

MISCELLANEOUS.

Institute of Chemistry.—*Pass List*: *March—April Examinations*.—Of eleven candidates who presented themselves for the Intermediate Examination of the Institute, seven passed:—J. D. S. Bramer; L. F. le Brocq, B.Sc. (Lond.); L. Davis, B.Sc. (Lond.); G. A. Stokes; S. H. Stroud; H. Trickett; and E. G. G. Wheeler. Of twenty-five candidates who presented themselves for the Final Examination, fourteen passed. In the Branch of Mineral Chemistry—S. C. Bate, B.Sc. (Lond.); F. G. Crosse; and S. G. Greene. In the Branch of Metallurgical Chemistry—E. Marsden. In the Branch of Organic Chemistry—W. F. Hollely; T. S. Jones, B.Sc. (Lond.); H. Lambourne. B.Sc. (Lond.); D. H. Peacock, B.Sc. (Lond.), B.A. (Cantab.); and F. Sproxton, B.Sc. (Lond.). In the Branch of the Chemistry of Food and Drugs, and of Water—A. L. Davidson; R. E. Griffiths, B.Sc. (Lond.); F. W. Hoyland; W. G. Saunders; and W. A. Storey.

Royal Institution.—On Thursday next, May 8th, at 3 o'clock, Mr. Edward Armstrong delivers the first of two ectures at the Royal Institution on "Florentine Tragedies," (1) "The Exile of Dante," (2) "The Burning of Savonarola"; and on Saturday, May 10th, Mr. H. A. Humphrey begins a course of two lectures on "Humphrey Internal Combustion Pumps." The Friday Evening Discourse on May 9th will be delivered by Mr. Frank Balfour Browne on "The Life History of a Water Beetle"; and on May 16th, by Captain Cecil G. Rawling, on "The Pygmies of New Guinea."

MEETINGS FOR THE WEEK.

MONDAY, 5th.—Royal Society of Arts, 8. (Cantor Lecture). "Antiseptics and Disinfectants," by David Sommerville.
—— Royal Institution, 5. General Meeting.
—— Society of Chemical Industry, 8. "Methods and Apparatus Used in Petroleum Testing—II., Viscometry," by W. F. Higgins. "Ore Deposits of Hu-Nan and Hu-Peh" and "Experiments on the Hydrometallurgical Treatment of Slimes," by W. R. Schoeller. "Hydrazinel Nitrate," by W. R. Hodgkinson.

TUESDAY, 6th.—Royal Institution, 3. "Recent Physiological Inquiries—Equilibrium and the Sixth Sense," by Prof. W. Stirling, M.D., &c.

WEDNESDAY, 7th.—Royal Society of Arts, 8. "Life Saving at Sea," by Axel Welin, Assoc. Inst. N.A.
—— Society of Public Analysts, 8. "New Apparatus for Maintaining Constant Temperatures," by F. H. and P. V. Dupré. "Proportionate Determination of Cocoanut Oil and Palm Kernel Oil in Mixtures," by H. R. Burnett and C. Revis. "Composition of Milk," by H. Droop Richmond. "Examination of the Oils from *Manihot ceara* and *Funtumia elastica* and a Comparison of their Properties with those of Linseed and Hevea Oils," by S. Rideal and L. H. D. Acland. "Recovery of Iodine from Residues," by H. W. Gill.
—— Faraday Society, 8. "Re-determination of the Elastic Modulus of Aluminium," and "Density of Aluminium," by F. J. Brislee. "The Potential due to Liquid Contact" (Part III.) and "Electrolytic Determination of Copper in Solutions containing Nitric Acid," by Elizabeth Gilchrist and A. C. Cumming. "New Experiments on Colloids," by T. A. Coward. "Overvoltage," by J. W. Richards.

THURSDAY, 8th.—Royal Institution, 3. "Florentine Tragedies—The Exile of Dante," by E. Armstrong, M.A.
—— Royal Society. "Various Inclinations of the Electrical Axis of the Human Heart," by A. D. Waller. "Trypanosome Diseases of Domestic Animals in Nyasaland—Part III., *Trypanosoma pecorum*," by Surgeon-General Sir D. Bruce, Majors D. Harvey and A. E. Hamerton, and Lady Bruce. "Excystation of *Colpoda cucullus* from its Resting Cysts and the Nature and Properties of the Cyst Membranes," by T. Goodey. "Experimental Hybridisation of Echinoids," by C. Shearer, W. De Morgan, and H. M. Fuchs. "Action of Radium Rays upon the Cells of Jensen's Rat Sarcoma," by S. Russ and Helen Chambers.

FRIDAY, 9th.—Royal Institution, 9. "Life History of a Water Beetle," by F. Balfour Browne, M.A.

SATURDAY, 10th.—Royal Institution, 3. "Humphrey Internal Combustion Pumps," by H. A. Humphrey, M.Inst.C.E.
—— Biochemical Society, 4. (In the Physiological Laboratory, Cambridge).

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Enquiry.—A correspondent wishes to have the addresses of producers of the following substances:—Tungstic glue, bakelite, copal gum, tragacanth gum, ammonium nitrate, calcium chloride, isinglass. —W. E. B.

The Soda Lake at Magada.—Sometime ago there appeared in the CHEMICAL NEWS an article on the soda lake called Lake Magada in south-east Africa. Can you inform us if this soda deposit is being worked, and also if there is a railway extending to it? We could find a market for the product just in the form that it is found in nature.—G. A. BRAUN, Secretary, National Chemical Company, Syracuse, N.Y., U.S.A.

THE SIR JOHN CASS
TECHNICAL INSTITUTE,
JEWRY STREET, ALDGATE, E.C.

Principal—CHARLES A. KEANE, D.Sc., Ph.D., F.I.C.

DEPARTMENT OF FERMENTATION INDUSTRIES.

THE CHEMISTRY AND TECHNOLOGY OF HOPS.

A Course of Five Lectures on this subject arranged for Brewers, Hop Growers, Hop Merchants, and others who are interested in Hops from the commercial point of view, will be given by

Mr. A. CHASTON CHAPMAN, F.I.C.

The Course will include a full description of the more important chemical constituents of the Hop, and a review of the present state of our knowledge in regard to their precise technological significance. An attempt will be made to indicate to the grower and merchant the nature of the Brewer's requirements, and to the Brewer the considerations which should exercise the greatest influence upon his judgment when buying.

The Lectures will be held on TUESDAY afternoons at 5 30 p.m., commencing TUESDAY, MAY 20th, 1913.

Detailed SYLLABUS of the Courses may be had upon application at the Office of the Institute or by letter to the PRINCIPAL.

THE CHEMICAL NEWS.

Vol. CVII., No. 2789.

NOTE ON THE ELECTROLYTIC DETERMINATION OF COPPER IN SOLUTIONS CONTAINING NITRIC ACID.*

By ELIZABETH GILCHRIST, B.Sc.,
and
ALEXANDER CHARLES CUMMING, D.Sc.

It is a matter of common experience that in the electrolytic determination of copper in solutions containing nitric acid it is impossible to deposit the last two or three milligrms. under ordinary conditions. J. H. Stansbie (*Trans. Faraday Soc.*, November, 1912) has shown that this is due to the presence of nitrous acid and that with a stationary electrode the accumulation of nitrous acid in the neighbourhood of the cathode causes dissolution of copper. "At first the current deposits the metal much faster than it is re-dissolved, but finally, when only traces of metal are present in the solution, dynamic equilibrium is attained, and no further permanent deposition of the metal can take place."

We might add to this statement that, with accumulation of nitrous acid in the solution, the rate of dissolution after some time often exceeds the rate of deposition.

Stansbie showed that with a rotating cathode satisfactory precipitation is obtained from solutions containing up to 3 grms. nitric acid per 100 cc. of solution and that addition of sulphuric acid was advantageous.

It appeared likely from Stansbie's results that, if the nitrous acid was destroyed by means of urea, satisfactory results would be obtainable with stationary electrodes. As a preliminary test, a solution was electrolysed which contained 0·508 grm. of copper and 10 cc. of concentrated nitric acid, diluted to 100 cc. The potential between the electrodes was 2·8 volts, and the current was passed for two hours. It was found that 0·120 grm. of copper was undeposited.

To a second solution 5 grms. of urea were added, the quantities and conditions being in all other respects identical with those in the first experiment; in this case only 0·009 grm. of copper remained undeposited after the two hours' electrolysis.

The addition of urea evidently produced a marked improvement, but from these experiments alone the results could not be definitely ascribed to removal of the nitrous acid. In these experiments the voltage was kept constant, but the current was not noted. In later experiments it was found that addition of urea raised the voltage between the electrodes (*i.e.*, lowered the conductivity of the solution) and caused a fall in the current. In all experiments deposition was much faster in presence of urea.

The following experiments confirm Stansbie's results as to the remarkable effect of nitrous acid in promoting the solution of copper by nitric acid, and prove that the urea acts by removal of the nitrous acid. Thin sheets of electrolytic copper of equal size were placed in the various solutions for three hours and the loss in weight determined. In each case the quantities given are for 100 cc. of solution; 10 cc. of ordinary concentrated nitric acid (sp. gr. 1·42) was added in each case, and the solution diluted to 100 cc.; the amount of nitrous acid given is the amount present per 100 cc. *before* addition of the urea.

Experiments 7 and 8 illustrate in a marked manner the effect of urea. Experiments 2, 6, and 8 show that there is little danger of copper dissolving if urea is present. In the electrolysis experiments the presence of urea is therefore very advantageous in minimising the risk of resolution at the end of the experiment. If a little urea is added when deposition is complete, the current can be stopped and the vessel washed out without any resolution of copper, provided that no unnecessary time is spent on the process. The consequent large dilution which results from the ordinary siphoning method of washing is thereby avoided.

No. of experiment.	Nitrous acid. Milligrms.	Urea added. Grms.	Weight of copper dissolved. Milligrms.
1	0·06	—	2·5
2	0·06	2	0·8
3	1·5	—	25
4	0·1	—	4·5
5	3	—	140
6	3	1	0·8
7	31	—	240
8	31	2	1·0

A number of experiments were made to find the best conditions for complete deposition with stationary electrodes. The electrolyses were performed in a platinum basin with a perforated platinum disc as anode. If the current used exceeded 3 ampères the deposit was usually spotted. With a potential difference between the electrodes of 2·5 to 3 volts and a current not above 3 ampères, beautiful coherent deposits were obtained. If the current was continued for any considerable time after deposition was complete the deposit usually became spotted. The following results show that complete deposition can be obtained even when the solution contains 10 cc. of concentrated nitric acid per 100 cc. of solution.

Cu present = 0·5080 *grm.*

1. 100 cc. of solution containing 10 cc. nitric acid and 5 grms. urea. Potential difference about 2·8 volts. Current passed for three hours. Cu found = 0·5090 grm. Error + 1 mg.

2. 100 cc. of solution containing 10 cc. nitric acid. Current passed for two hours without urea; then added 2 grms. urea and passed current again for one hour. Potential difference from 2·5 to 2·8 volts. Cu found = 0·5080 grm. Error less than 1 mg.

Chemistry Department, University of Edinburgh.

* A Paper read before the Faraday Society, May 7, 1913.

SOME INDUSTRIAL USES OF SUGAR.

Many Important Uses for Sugar for other than Food Purposes—Great Diversity of Manufactures into which it Enters.

By GEORGE W. ROLFE.

Sugar—using the term quite in the popular sense, meaning what the grocer calls sugar—is of enormous importance to mankind as food, its annual consumption of some 17,000,000 long tons is enough to give every inhabitant of the earth at least 20 lbs. Hence, the attention of most people is diverted from the numerous uses of this substance in many large industries, by no means alimentary.

M. Vivien has given a most informing paper on this subject in recent numbers of the *Bulletin de l'Association des Chimistes de Sucrérie et de Distillerie de France et des Colonies*, the leading French sugar periodical. Vivien writes with special reference to conditions in France, his paper being a plea for the use of sugar as the cheapest form of a chemically pure carbohydrate, replacing in many cases glucose, starch, and dextrin.

The French Government imposes an internal revenue tax on sugar and glucose products used as human food which makes the price of sugar about 12 cents per pound, but by a law similar to that which applies to alcohol in this country "denatured" sugar, that is, sugar to which some substance has been added to make it unfit for food, is exempt from taxation. As in alcohol denaturising, the

substance added is, if possible, some ingredient in the special process using the sugar.

In France, an excellent quality of sugar known as No. 3 white sugar and polarising over 99 per cent sells, when denatured, at a price equivalent to from 3 to 4 cents a pound, or about what the refiners pay here for raw sugar. This is lower than starch, glucose, or dextrin sells in Europe.

It may be of interest to note some of the more important applications of this denatured sugar, bearing in mind that in this country at present market conditions molasses and starch products are more economical substitutes in some cases. Some of the industries which Vivien enumerates are large consumers of sugar in this country.

Sugar is a common ingredient of many compounds for removing and preventing boiler-scale. As these usually contain alkali, this is used as a denaturant. The shoe blacking industry uses sugar and molasses to considerable extent. In Europe there seems to be a tendency to use blackings of this older type as less injurious to leather than the newer wax blackings, owing to the solvents used in the latter. These shoe-blackings are made by the carbonising action of sulphuric acid on the sugar. The product is neutralised, and other ingredients added, such as powdered boneblack, oil, ink, and sometimes glycerin.

Perhaps one of the industries of greatest present importance, both here and in France, is the manufacture of transparent soap. Originally, the English soaps were made by the costly process of dissolving the soap in alcohol, decanting the soap solution, and recovering the alcohol by distillation. Later, glycerin was used as a solvent, but this made the soap too sticky, so that it soiled the wrappers. The sugar soaps do not have this disadvantage. Hence, many tons of sugar are now used by soap manufacturers in this country as well as in Europe.

There are over thirty patents for explosives in which sugar is a component to the extent of from 6 to 40 per cent. This use of sugar has been so important in Germany that a special provision is made by that country for denaturising sugar used in the manufacture of explosives, paraffin or similar oil being used.

In the colour and dyeing industries we find sugar used as a reducing agent in indigo and chrome work, as a base for the manufacture of organic chromium salts, and as a vehicle or "filler" for solid aniline colours, giving them an attractive appearanee. In many cases this latter practice is carried to somewhat questionable lengths, as some of these dyes contain over 90 per cent of sugar.

So, too, the European tanneries use large amounts of sugar in "filling" leather (glucose being used in this country) and, to some extent, in removing lime from hides in the "dehairing." This solvent action of sugar on lime and the easy recovery of the sugar by carbonation, has suggested its use in several processes where it is desirable to remove excess of caustic lime from calcined minerals, such as phosphates, zinc, or magnesium oxides, and the like.

Tannin extracts are also "filled" with sugar, as they are on this side of the water, with glucose. Sugar is also used in several chrome tanning processes as a reducer, and, as in dyeing, for making acetates and formiates.

Ordinary copying ink is made by the addition of 1 part of sugar to 3 parts of writing ink. Printer's rolls and hektograph pads are made from glue combined with sugar or molasses. The silvering of glass mirrors is another important industry in Europe. Sugar, after inversion with acids, is here used to reduce an ammoniacal solution of silver nitrate which deposits a coating of silver on the glass immersed in the solution.

The hardening and strengthening action of sugar in mortar was known to the ancients in the far East, and it is said that the Romans also made use of saccharine solutions for this purpose, although sugar, known as "Indian salt," was rarely seen in the Empire. Some of this ancient masonry containing sugar still stands in good condition.

In recent times, the Museum of Natural History in Berlin has been rebuilt with mortar consisting of 1 part of lime, 1 part of sand, and 2 parts of sugar. Sugar is also used for hardening plaster moulds.

In many chemical operations, sugar is used as a source of carbon of high purity, such as in the manufacture of pure carbon monoxide or sulphurous acid. As to future application it is possible that sugar may become of great industrial importance through its nitro-compounds. Nitrosaccharose (sucrose octonitrate) is a product analogous to gun-cotton, which, it is said, can replace the latter in its numerous applications in explosives, collodion, celluloid, and the like. Similarly, it is claimed, sucrose acetate can take the place of the corresponding cellulose compound in viscose and artificial silk.

Certain compounds of sugar and benzoic acid also show promise in this direction.

This list of industrial applications of sugar is by no means exhaustive, but perhaps suffices to illustrate the great diversity of manufactures in which this product appears quite apart from food economy.—*Science Conspectus*, iii., No. 2.

THE QUANTITATIVE SEPARATION AND DETERMINATION OF SUBSIDIARY DYES IN THE PERMITTED FOOD COLOURS.

By WALTER E. MATTHEWSON,
Assistant Chemist, New York Food and Drug Inspection Laboratory.

MOST simple commercial dyestuffs contain large amounts of subsidiary colouring matters. The percentage of such substances in the purer dyes intended for use in food products is a matter of some importance, as they may constitute the most objectionable of the impurities. Reasonably pure colouring matters are necessary in examining methods for the estimation of the subsidiary colouring matters. A brief description is here given of the pure colours employed in this work. All were made in the laboratory from "chemically pure" grade chemicals of high quality, unless otherwise stated. The dyes were given a second crystallisation, or salting out, and seemed to be practically free from organic impurities.

Orange I. — From diazotised sulphanilic acid and α-naphthol.

Orange II.—From diazotised sulphanilic acid and β-naphthol.

Ponceau 3 R.—From diazotised 1-2-4-5-pseudo-cumidin (melting-point, 63° C.) and commercial R-salt (sodium salt of 2-naphthol-3-6 disulphonic acid), the latter purified by boiling out with 80 per cent alcohol, and crystallising from salt solution and from water.

Crocein Orange.—From diazotised anilin and commercial S-salt (sodium 2-naphthol-6-sulphonate), the S-salt purified by crystallising from salt solution and from water.

Amaranth.—From diazotised naphthionic acid and R-salt prepared as stated for ponceau 3 R.

Fast Red E.—From diazotised naphthionic acid, and S-salt, the latter similar to that used for crocein orange.

New Coccin.—From diazotised naphthionic acid and commercial G-salt (sodium salt of 2-naphthol-6-8-sulphonic acid) purified by crystallisation from water.

Determination of Fast Red E *and Similar Colours in Amaranth.*

This separation is readily made by the procedure indicated in Bureau of Chemistry *Circular* 89. Treat the solution containing about 0·2 grm. dye with 5 cc. five-normal hydrochloric acid and dilute to 50 cc. Then shake out with amyl alcohol, extracting in succession in three separatory funnels, each containing 50 cc. of the solvent. Wash the amyl alcohol portions in the funnels with three 50 cc. amounts of fourth-normal hydrochloric acid, these being passed through the series in the same order as was

the original solution. Give the last two separators a fourth washing, the last one a fifth. Then dilute the amyl alcohol with gasoline, removing the fast red with very dilute caustic soda solution, and determining by the method of Knecht and Hibbert, using titanium trichloride. With large amounts of fast red a series of four funnels must be used. In all cases it is essential that the liquids be thoroughly shaken together.

The results obtained by this method follow:—

Determination of Fast Red in Amaranth.

Number of funnels.	Total dye taken. Grm.	Fast Red taken. Per cent.	Fast Red recovered. Per cent.
3	0·1644	0·0	0·15
3	0·1737	5·3	5·2
3	0·2107	22·0	21·3
4	0·2107	22·0	22·0

Approximate figures may be obtained by diluting 2·5 cc. of the 1 per cent solution of the dye with 30 cc. of fiftieth-normal hydrochloric acid and shaking with 15 cc. of amyl alcohol. The amyl alcohol is then compared colorimetrically with standards prepared in the same way, using pure dyes or those of known composition.

Approximate Determination of New Coccin and Similar Dyes in Amaranth.

The following empirical method gives a measure of the amount of such colours present:—Treat 50 cc. of the 0·02 per cent solution of the colour with 10 cc. of tenth-normal benzidine solution (9·2 grms. base per litre, in half-normal hydrochloric acid), mix the solution well, and allow to stand exactly two minutes. Then filter through a folded filter and titrate 50 cc. of the filtrate against titanium trichloride. Blanks made up with known amounts of pure amaranth and new coccin are carried through at the same time. As Fast Red E and similar colours interfere, if this method has been used for their separation, the extracted solution and washings containing the amaranth are combined and taken to dryness on the water-bath to remove the acid and dissolved amyl alcohol. This evaporation does not affect the amaranth.

Advantage may also be taken of the lability of the 6 sulpho-group in amaranth, when warmed with potassium cyanide solution (see Lange, D.R.P. 189935 and 191838):—Treat 20 cc. of the 1 per cent solution of the dye with solutions containing 1 grm. each of potassium cyanide and ammonium chloride, and make the volume to 45 cc. Heat the mixture for six minutes in a large test-tube immersed in a boiling water-bath. Then quickly cool and acidify by addition of 10 cc. of concentrated hydrochloric acid. The amaranth (colour acid) is converted into sulpho-naphthalene-azo-2-naphthol-3-cyan-6-sulphonic acid, a maroon dye that may be separated from the unchanged new coccin by a procedure similar to that described for Fast Red E. Some colouring matter is destroyed, and it is necessary to carry through blanks containing known amounts of the dyes.

Determination of Monosulphonated Dyes in Ponceau 3 R.

The separation of the monosulphonated orange dyes from ponceau 3 R by means of amyl alcohol and dilute hydrochloric acid gives high results for the orange, which becomes especially apparent when one of the colours is present in relatively small amount. This is due to the fact that the distribution ratio of ponceau 3 R changes rather markedly with varying dye concentration, in dilute mixtures the colour becoming relatively more soluble in the alcohol layer. Consequently it is practically impossible to wash out the last traces of ponceau from the solvent containing the orange. An accurate separation may be made, however, by using first dilute acid to remove the bulk of the ponceau, completing the washing with 5 per cent sodium chloride solution. The first washings with the salt water may contain some ponceau in suspension, but the amount is so small that it does not interfere. It is hardly advisable to use hydrochloric acid of lower concentration than sixteenth normal, as even at this strength the liquids separate rather slowly.

The monosulphonated dye present in commercial ponceau 3 R is perhaps mainly sodium trimethylbenzene-azo-naphthol-sulphonate, derived from diazotised pseudo-cumidin and S-salt. Instead of this colour, crocein orange was used in the work described below, a pure lot having been prepared some time previously for another purpose. Since with homologous dyes the relative solubility in amyl alcohol seems to increase with the molecular weight, a separation effective for crocein orange should be still more so for its homologues, although the differences here are insignificant.

A procedure similar to that described for Fast Red E was followed. The dye solution was treated with 2·5 cc. five-normal hydrochloric acid diluted to 50 cc., and then passed through three funnels, each containing 50 cc. amyl alcohol. Four 50 cc. portions of sixteenth-normal acid were then passed in order through the separators, followed by three 50 cc. portions of 5 per cent salt solution. The last two separators were washed with a fourth 50 cc. portion of the salt solution, the last one with a fifth. The dye was then removed as stated below.

Determination of Orange in Ponceau 3 R.

Total dye taken. Grm.	Orange taken. Per cent.	Orange recovered. Per cent.
0·1867	0·0	0·2
0·1961	4·8	5·0
0·2339	20·5	20 2

Determination of Orange II. *in Orange* I.

In the preparation of these dyes it is known that orange I. is much more soluble than orange II. in dilute sodium carbonate solution. They may be separated by a method similar to that described for Fast Red E, using amyl alcohol and 5 per cent sodium carbonate solation. The equilibrium between the concentrations of the orange I. in the two layers is not very quickly established, and the mixtures must be well shaken, then given some time to separate. The liquids can be very quickly separated with a centrifuge.

The following procedure furnished the data given. The dye solution (about 50 cc.) was treated with 10 cc. concentrated hydrochloric acid and shaken with 50 cc. amyl alcohol. Practically all the dye went into the alcohol, and the lower layer was drawn off and discarded. The amyl alcohol was then washed with six 50 cc. portions of normal or 5 per cent sodium carbonate, these being passed successively through a second and third funnel, each containing 50 cc. of amyl alcohol. The last two funnels were given two additional washings. Gasoline was then added, and the colour removed and determined in the usual way.

The result given in the fourth line was obtained by the same procedure, except that a third funnel was not used.

Determination of Orange II. *in Orange* I.

Total dye taken. Grm.	Orange II. taken. Per cent.	Orange II. recovered. Per cent.
0·1605	0·0	0·3
0·1708	5·7	6·0
0·2095	23·4	22·6
0·1708	5·7	5·5

Determined by these methods in the dyes intended for sale as food colours, amaranth contains from 1 to 5 per cent lower sulphonated colours, and somewhat more new coccin and similar dyes. Ponceau 3 R contains from 1 to 5 per cent lower sulphonated dyes, and orange I. the same amount of orange II. *Circular* No. 113, Bureau of Chemistry, U.S. Department of Agriculture.

THE CONTROL OF TEMPERATURE IN THE OPERATIONS OF ANALYTICAL CHEMISTRY.*

By THEODORE W. RICHARDS.

THE control of temperature is a very important question in the work of the analytical chemist. The reason is at least three-fold. In the first place, temperature affects greatly the speed of all chemical reactions, which are generally accelerated to extents varying perhaps seven to twelve per cent by each degree's rise in temperature. In the second place, temperature affects the final equilibrium attained by many reacting systems, and therefore influences both the yield and the composition of the products dealt with by the analyst. In the third place, accurate physical measurements, to which the quantitative experimenter must frequently resort—such as weighing the measurement of the volumes of gases and liquids, and the determinations of calorimetric or electrical magnitudes—demand considerable control of temperature if any accuracy is sought.

Clearly, the subject is too large for the brief ten minutes to be devoted to it; but a few words may be able to point out the more vital features.

Let us begin with the control or temperatures near that of the room. In the first place, it is clear that every chemical laboratory may advantageously have a thermostat attachment to its heating arrangements. For years I have used a commercial contrivance which, when operating properly, has kept my laboratory at 20° C. within half a degree, greatly to my satisfaction. In order to attain any such constancy, the air of the room must be efficiently agitated by means of an electric fan; just as any other form of thermostat should be adequately stirred. Of course, when an operation affected by currents of air is undertaken, the fan must be temporarily stopped.

Entirely within this room, surrounded by glass walls and without any outside windows, is built a balance-room, which resembles a huge balance case; and this remains constant for long periods within one or two-tenths of a degree, because the somewhat larger fluctuations of the outer room do not quickly pass through the glass walls. The plan has worked so excellently that all balance-rooms in the new Wolcott Gibbs Memorial Laboratory at Harvard are to be built in this way entirely within other rooms.

A very suitable, sensitive, and easily constructed thermostat attachment for regulating the temperature of a room is the sealed hydrogen manometer, with electrical contact (Regand and Fouillard, *Z. wiss Mikroscop.*, 1903, xx., 138; also Richards and Mark, *Proc. Am. Acad.*, 1905, xli., 119). This consists of a large sealed bulb containing hydrogen, which gas is arranged to support a column of mercury having an electrical contact at its upper end—the affair is a combination of a gas thermometer and a barometer. The rapid heat conduction in hydrogen makes this gas especially suitable for the purpose. We have used the device for many years with great profit, and by its aid have been able to keep a cellar laboratory, which is protected by double windows, within 0·1 degree for weeks at a time. The electrical current, made and broken at the mercury surface in the top of the manometer by the fluctuations of the expanding or contracting hydrogen, may be made to operate a relay which in turn regulates the heating apparatus, whether this uses steam, hot air, gas, or electricity. A form in which the current running through the mercury in the manometer itself is used for heating has recently been described (Bousfield, CHEM. NEWS, 1912, cv., 13), but I should be afraid that this might not be able to maintain quite as accurate a constancy as an apparatus using a weaker current in its regulating manometer.

Often the yet more accurate regulation of the temperature of small objects is needed; of course the Ostwald toluene regulator in a bath of water or oil gives the most convenient thermostat for such purposes. Of late we have used, on account of its cleanliness and safety, only electricity as a means of supplying heat to this bath; the regulator is arranged so as to make and break a feeble electrical circuit which operates a relay through which in turn runs the stronger heating current. The chief, probably the only disadvantage of electrical heating, is the possible leakage of electricity. If it is used for electrochemical work, one must guard against stray electromotive forces by efficiently grounding the thermostat. The description of an arrangement of this kind making possible the maintenance of the temperature within 0·001° or 0·002° for days is perhaps not out of place. This has been used at Harvard for many years; it was briefly described several years ago and has been used independently by others (Richards, Carnegie Inst., Washington, 1906, *Pub.* lvi., 22; 1907, lxxvi., 9).

The thermostat consists of a large can which may be as large as 70 cm. in diameter and 70 or more high. The can is covered on the outside with felt and may have its surface protected with oil if evaporation is to be prevented. Within this can is immersed a regulator similar in principle to the toluene thermostat regulator of Ostwald. The receptacle for the toluene is made with five large fingers having walls of moderately thin glass, and is arranged to have a capacity of over half a litre. The mercury column, raised and lowered by the expansion or contraction of this toluene, "makes" and "breaks" a feeble electrical circuit which governs through a relay the stronger current used for heating. The latter current passes through the relay and through a large insulated heating coil immersed deeply in the water of the thermostat.

The "making" and "breaking" happen advantageously in a somewhat narrow tube, perhaps two millimetres in diameter, and the mercury in this tube should be protected from the laboratory air by an atmosphere of pure hydrogen, supplied by a very small automatic hydrogen generator attached to the apparatus. This device is very important if great constancy is sought; it constitutes the only unusual feature of our apparatus.

The efficiency of this regulator, or indeed of any other, as a means of keeping the temperature constant depends greatly upon the agitation of the water in the thermostat. This should be violently stirred by means of a rather powerful motor in order to keep the temperature constant throughout and to effect a rapid exchange of heat between the bath and the toluene regulator. The degree of agitation usually employed is entirely inadequate. The temperature is obviously much more constant if the room containing the thermostat is allowed to vary but little in temperature; it is advantageously kept perhaps a degree below the temperature of the bath. By running a thin pipe containing cool water around the inner circumference of the top of the bath, compensation for a higher temperature may be easily obtained. If care is taken and the glass toluene receptacle is sufficiently large, and is well seasoned so that it has assumed a reasonably constant volume, the thermostat will keep constant within one or two-thousandths of a degree for weeks.

This arrangement makes no pretence to novelty in principle, but in efficiency it probably exceeds most other forms because of the details needed in its construction. A very similar apparatus has been more recently described by Hulett (*Physical Review*, 1911, xxxii., 277), but he does not seem to have sought or attained quite the degree of precision which we have successfully employed.

Very satisfactory thermostats may be made from baths filled with pure salts in the act of transition from a state of greater to a state of less hydration. Such mixtures keep a striking degree of constancy for a long time. Sodium sulphate is the best substance for this purpose. For details a paper by K. L. Mark and the present author in Vol. 38 of the Proceedings of the American Academy of Arts and Sciences should be consulted.

* Paper presented at the Eighth International Congress of Applied Chemistry, New York.—From the *Journal of Industrial and Engineering Chemistry*, iv., No. 12.

The control of low temperatures and of high temperatures has received so much general notice recently that this expert audience needs no detailed exposition of these topics. The employment of pure ice for maintaining a definite degree of coolness is known to every one, but the almost equally serviceable use of ice mixed with solutions of definite concentrations for increasing coolness is perhaps less generally recognised (this was suggested by Roloff, *Z. phys. Chem.*, 1895, xviii., 572).

For example, ice mixed with dilute hydrochloric acid containing 28·19 grms. of hydrogen chloride per litre gives a perfectly constant temperature of −3·00° (Richards and Jackson, *Proc. Am. Acad.*, 1906, xli., 473). Of course, if heat is added, some of the ice melts, the solution becomes more dilute, and the temperature rises. This, however, may be easily prevented by enclosing the constant-temperature bath by another bath containing a mixture having the same freezing point. If an air space (or still better, the evacuated space of a Dewar vessel) is placed between the two baths, the inner one will maintain an amazing degree of constancy for long periods of time, particularly if more dissolved substance from time to time is added to the outer vessel as its ice melts. The lower limits of the temperature attained in this way are of course the cryohydric temperatures of the more soluble substances.

Lower temperatures are customarily obtained by means of solid carbon dioxide with alcohol or ether, and still lower ones by liquid air and hydrogen. By boiling the liquefied gases under reduced pressure their temperature-range may be extended considerably. The details of working with these now familiar substances need hardly find a place in this brief review. Acquaintance with the necessary technique is becoming more and more an essential part of the complete chemist's outfit, although analytical operations rarely demand low temperatures.

Turning now to higher temperatures more frequently employed by analytical chemists, wide limits must receive consideration. Open steam baths are essential, and are too well known to need discussion. Thermostats of concentrated salt solutions or oil or paraffin, or of fused mixed sodium and potassium nitrate, may be used at fairly high temperatures, if proper regulating devices are employed. For most purposes, however, air baths regulated either by thermostat control or by approximately constant steam, gas, or electrical heating are more commonly employed. If steam under constant pressure is available, it forms a very usual and convenient means of maintaining constant temperatures somewhat above 100° of the needed in analytical laboratories. Gas, or more recently, electrical heating, is more commonly used; the latter has the great advantage of cleanliness. Other vapours also, such as toluene (100°), the xylenes (140°±), and aniline (184°) are often used with advantage. Air baths without thermostat attachments are usually arranged to maintain only a certain difference between the room temperature and the higher temperature sought. This is all very well if the room remains constant in temperature, but sometimes laboratories change as much as 10°,or 15° during the day, and this change may have serious effects in some delicate operations when it reappears in the heated air bath. For such operations a thermostat regulation of the temperature of the bath is almost essential.

The forms of air bath which have been proposed are countless. Most of them lack the needful requisites of resistance to corrosion and therefore of cleanliness. The utensils containing the substance to be heated usually need to be protected by some form of shelter or roof, such as a watch-glass, to keep out particles of impurity from the corroded walls of the oven. This is altogether unfortunate; the air bath used by analysts should be free from such defects, therefore it should be made of glass or porcelain (a simple, clean, and inexpensive electric oven is described in *Am. Chem. Jour.*, 1899, xxii., 45). It is almost needless to point out that for many purposes the products of combustion also should be rigidly excluded from the inside of the oven if gas is to be used as a source of heat. Moreover, the air of the laboratory is often injurious to sensitive substances; such material should be heated in boats within tubes, even if only dried at 100°. The well known "bottling apparatus," so much used at Harvard, makes this precaution easy (see, for example, the Faraday lecture of 1911, *Jour. Chem. Soc. Trans.*, xcix., 1203).

For higher temperatures burners of various shapes are available, and more and more use is being made of the yet greater possibilities of electrical heating.

Most of the gas burners are either modifications of the Bunsen burner or the blast lamp, and some of the former, especially the Meker burner, have been made of such efficiency as to replace for many purposes the use of air under pressure. To obtain a constant temperature with these burners, it is necessary usually to attach to the gas supply a contrivance for giving it constant pressure; otherwise the fluctuations are considerable. It is needless to point out that contrivances for preventing radiation, such as clay cylinders and other forms of furnaces, greatly promote the constancy of temperature attained.

Turning now to electric heating, we have not only the electric furnace so much used in technical work, but also, more suitable for analysts, a sort of electric muffle, a porcelain, or other refractory tube wound with resistance wire, capable of producing and withstanding the high temperatures needed. For temperatures up to 1000° the alloy called "nichrome" works very well as the material of the resistance wire; for higher temperatures platinum is necessary, but even that is less refractory than one might wish. We have obtained excellent results with the type of furnace made in this fashion with tubes of pure silica as core. The maintenance of constant voltage and even conditions of radiation provides the operator with a very fairly constant temperature, which is most conveniently estimated by the platinum-rhodium thermopile.

In summing up, it may be said that attention has been called to the relative advantages and fields of usefulness of some of the more important methods of controlling temperatures between 3000° and —250°. A few of the most essential details of execution have been suggested, and emphasis has been placed upon the frequent importance of constancy of temperature and of the exclusion of outside impurity.

THE LATEST ACHIEVEMENTS AND PROBLEMS OF THE CHEMICAL INDUSTRY.*

By CARL DUISBERG.

(Continued from p. 210).

Sulphuric Acid.

The triumphal progress of the contact process for the manufacture of sulphuric acid in the United States scarcely has its parallel in Germany, where it originated. Platinum, in spite of the fact that its price has increased three-fold, is still our principal contact agent. As it is possible to carry out other contact processes with various contact materials, we shall certainly find other agents than platinum available for sulphuric acid anhydride. It ought therefore to be a fruitful field for research to find cheap substitutes for platinum. In the twenty years that have elapsed since Knietsch first successfully carried out the contact process, the Americans have increased their output three-fold for the same weight of platinum. Nevertheless, the old lead-chamber process still competes with the new method, and the steady improvement of this process and the purity of the resulting acid must be acknowledged. In fact, the lead-chamber process promises to make further progress in

* From the *Journal of Industrial and Engineering Chemistry*, iv., No. 10.

the future in view of the success of Falding's high chambers and Opls towers in which large quantities of acid flow down.

The Gaillard tower is supreme for concentration and recovery of the acid and for the regeneration of the various waste acids.

Ammonium Sulphate.

A new way of manufacturing sulphuric acid, together with ammonia, from the gases which are produced by the dry distillation of coal, is looming above the horizon. Burkheiser is seeking, with the aid of especially prepared wet iron compounds, to bind the sulphur, simultaneously absorbing cyan, and to convert the ammonium sulphite thus produced into ammonium sulphate by oxidation with atmospheric air.

In competition with Burkheiser, Walter Feld is endeavouring to recover sulphur directly as ammonium sulphate by a series of interesting reactions, in which thiosulphates play an important part. Such plants are in operation in Königsberg and here in New York.

Nitrogen Compounds.

So much has been written concerning the progress made in the last five years in the utilisation of atmospheric nitrogen, that I need not enter into a description of Birkeland-Eyde's, Schonherr's, or Pauling's process for the direct oxidation of nitrogen by means of the electrical discharge, nor of Frank-Caro's method of forming cyanamide from carbides [the world production of cyanamide is, according to Dr. N. Caro, 120,000 tons per year, of which 31,000 tons are manufactured in Germany (16,000 in Trostberg and 15,000 in Knapsack near Cologne), 19,000 tons are made in Niagara Falls by the American Cyanamide Co., and during the next three years the total production is to be increased to 200,000 tons], nor is it necessary to describe the Serpek process for the production of ammonia from aluminium nitrides combined with the utilisation of alumina which is simultaneously obtained. I will mention, however, that the problem of concentrating the dilute nitric acid, as obtained in the large absorption apparatus from nitrous gases, has been solved by Pauling's method, in which sulphuric acid is used in a battery of towers. It is also possible now to economically convert cyanamide into ammonia and this again into nitric acid.

Soda and Chlorine.

The fifty year old Solvay process, which has conquered the whole world, still remains master of the situation. This is all the more remarkable since it is still imperfect as far as the yield is concerned; a quarter of the salt used in the process is lost as such and the whole amount of chlorine in the form of calcium chloride.

Although the materials employed in the LeBlanc process are completely utilised, this fact will not give it any chance of surviving, and it would seem to be now chiefly of historical interest.

Not less remarkable is the twenty five years' career of the alkali-chloride electrolysis. The limited market for chlorine compounds and the great space taken up by the electrolysing baths were great obstacles to the progress of this apparently simple method. For the same reasons the most approved processes, such as the Griesheim's cement cell, the quicksilver cathodes of Castner and his successors, the Aussig Bell and the wire-gauze diaphragm of Hargreaves, with its many varieties, of which the Townsend cell is the latest and best, did not develop as expected. The limited demand also quickly restricted the operation of the brilliant method of manufacturing chlorates by electrolysis.

Tin.

Tin is not only produced from natural ores, but also in more than twenty detinning establishments from tin-plate nd tin-can waste; 200,000 tons of tin-plate waste are subjected to this treatment and about 24 million marks (6,000,000 dols.) worth of tin and iron are recovered. The electrolytic detinning process, on account of high wages, the great cost of current, and the considerable manufacturing loss, has been replaced—where there is a market for chloride of tin—by the patented process of Thomas Goldschmidt, of Essen. This process takes advantage of the properties of chlorine gas, in the dry state, to greedily take up tin without reacting on iron if certain temperatures are observed. Instead of the inferior quality of electrolytic tin mud, which must be converted into marketable tin by costly smelting operations, the new process yields an anhydrous tin chloride used in large quantities for weighting silk. The detinning with chlorine is not carried out with cuttings, as in the electrolytic process, but with waste pressed in hard packages so that twenty times as much material can be treated in the apparatus at the same time. In the United States this process is operated by the Goldschmidt Detinning Company of New York.

Reducing and Oxidising Agents.

One of the most brilliant successes in applied chemistry has been achieved by the persevering experiments of some chemists with a long neglected substance, the constitution of which had never been properly understood. The old hydrosulphite of Schützenberger, rendered stable and easily transportable in powder form as an anhydrous sodium salt or as rongalite in combination with formaldehyde, has now become a most important article of commerce. It is chiefly used in vat dyeing and for reducing purposes in general, such as stripping dyed fabrics and as decrolin for bleaching sugar.

Peroxides, Persulphates, and Perborates.

Peroxide of hydrogen and and its derivatives at present find less favour in commerce, although their future appears to be very brilliant. Recently the Farbenfabriken vorm. Friedrich Bayer and Co. succeeded in rendering this important oxidising agent, which easily decomposes and can be marketed only in water solution, solid and stable by the addition of urea.

This powder is in the market under the name of Ortizon, but on account of its relatively high cost is intended not so much for technical as for hygienic and pharmaceutical purposes.

The interesting manufacture of sodium peroxide from sodium and the many scientific investigations of the persalts, have not been followed by great commercial success. The persulphate and perborate, however, the latter under the name of "Persil," are being manufactured on a large scale. The reason of this failure seems to be the high cost of production.

Rare Metals.

The most interesting alloys discovered by Muthmann and Auer have found little application in the arts, and the use of cerium and thorium preparations is still confined to the incandescent gaslight industry. Only the "Auermetal," consisting of 35 per cent iron and 65 per cent cerium, is employed, and this only to a limited extent for the manufacture of pocket cigar lighters.

In the metal filament lamp industry, tungsten, which shows the highest melting-point of all metals, namely, 3100° C., has replaeed tantalum, which melts at about 2300° C. This became possible only after successful experiments to render the metal ductile by hammering.

The elements cadmium, selenium, and tellurium are obtained in great quantities as by-products; the first is produced in the zinc industry, and the other two from the Tellur gold ores found in Cripple Creek, Colorado. Although sold at relatively low prices they find but little use in the industries.

Artificial Precious Stones.

Finally, I will, in but a few words, touch upon a new industry, viz., the synthetic manufacture of precious stones from alumina with additions of chrome oxide, iron oxide, or titanic acid. Artificial rubies and white, yellow, and blue sapphires, which cannot be distinguished from natural

stones, are being manufactured in great quantities in Paris, and recently also by the Electrochemische Werke, Bitterfeld. They are used extensively for jewellery, and especially as bearings in watches and measuring instruments.

All this will give you a striking picture of the development of inorganic chemistry which is taking a more and more important position beside organic chemistry.

Applied Organic Chemistry.

In the organic chemical industry the reactions are considerably more complicated and the apparatus mostly smaller than in the inorganic industry. Here the chemist, like a juggler with his balls, gives every atom a definite position in the many thousand combinations which carbon forms with hydrogen, oxygen, nitrogen, and sulphur, and there exist the most varied reactions and processes which may lead to the same result. This chemistry of the carbon compounds has been most wonderfully perfected in the coal-tar colour industry, and in every factory of this branch there are hundreds of scientifically trained chemists always experimenting and daily finding new combinations possessing properties of technical value. Before these products become finished articles to be sold as colours, perfumes, or pharmaceutical preparations, they must further go through a series of numerous intermediary operations, which finally lead to the marketable chemicals.

Coal-Tar.

The starting material of the important coal-tar colour industry is the black tar which is obtained by the dry distillation of coal, and is known to contain about a hundred and fifty different chemical products, of which, aside from carbolic acid, the aromatic hydrocarbons, benzole and its homologues, toluol and xylol, naphthalene and anthracene, play the greatest part.

More recently carbazol has been isolated from tar on a large scale, and has become a most important raw material for the manufacture of the colour "Hydronblue" by Leopold Cassella and Co., Frankfort a/M. Hydronblue is a sulphur dyestuff distinguished by its fastness against washing and chlorine. Acenaphthen, which also occurs in coal-tar as such, is the starting material of a red vat dye "Cibanonred," discovered by the Society of Chemical Industry in Basle. It is to be regretted that hitherto no technical use has been found for phenanthrene, which is also one of the constituents of tar.

Besides carbolic acid, its homologues, and the various cresols, &c., are being isolated by Dr. F. Raschig in Ludwigshafen on the Rhine. These substances are largely employed in the manufacture of explosives and colouring matters.

As long as coal-gas is produced for illuminating and heating purposes, and as long as coke must be used for the reduction of iron ores, tar will always remain the cheapest raw material for the manufacture of these hydrocarbons. But since it may become necessary in the future —as is already possible to-day—to use coal in a more rational way, at the same time producing hydrocarbons, the coal-tar colour industry need not fear a scarcity of this important raw material, the less so as certain kinds of petroleum, *e.g.*, Borneo petroleum, contain large quantities of aromatic hydrocarbons from which the Rheinische Benzinwerke, in Reisholz, near Düsseldorf, has already isolated toluene in the form of nitrotoluene in a commercial way. If, however, a still greater demand for these hydrocarbons should occur, other methods of obtaining them must be found. We shall then surely succeed in producing them synthetically either directly from the elements carbon and hydrogen, or indirectly from carbide of calcium by passing acetylene through glowing tubes—a reaction which was already carried out successfully in the early sixties of the last century by Berthelot, and recently by Richard Meyer. At the present time about one quarter of Germany's annual output of coal is converted into coke, viz., 20 per cent for foundry purposes and 4 per cent in gas works, while in England the quantities are 12 per cent and 6 per cent respectively.

Distillation of Tar.

The point of greatest importance in the distillation of tar is still the separation and isolation, in the cheapest possible way, of the different hydrocarbons in their purest form. The stills have been continually enlarged, those employed to-day having a capacity of 60,000 - 80,000 litres (13,000—17,500 gallons). On the other hand, a continuous process, such as is possible in the bituminous coal-tar industry, has not yet been found. A large number of patents have been taken out for apparatus intended to solve this problem, but none of them have proved satisfactory in practice.

(To be continued).

HOW TO TELL THE ARTIFICIAL SILKS.

Artificial silk is fast coming to be a very important textile material and is being used in ever increasing quantities by the trade. It is employed as an adjunct not only to the silk industry itself but is also being used in connection with wool and cotton in the preparation of a great variety of fabrics. It is even being used largely in knot goods and hosiery in combination with cotton and mercerised cotton.

The dyer therefore is meeting more and more with this product, and as there are three different kinds of artificial silks in general use, and as these different varieties possess certain differences in structure and quality, it really becomes a question of considerable importance to the dyer to know one variety from another. This is more especially important because one silk may stand a treatment which would be fatal to another.

The three artificial silks now to be met with on the market are described in a recent issue of the *Wool and Cotton Reporter* as follows:—

1. Collodion silk, known as Chardonnet, or nitrosilk. It is prepared from nitrated cotton.

2. Cuprate silk, known as Glanzstoff, Pauly, Elberfeld silk. It is prepared from a solution of cellulose in cuprammonium solution.

3. Viscose silk. This is prepared from a solution of cellulose in a mixture of caustic soda and carbon bisulphide.

In their outward appearance the three forms of artificial silk are so nearly alike that it would not be possible to distinguish between them. Even a microscopic examination by an experienced observer does not lead to any positive conclusion as to kind of silk.

A fairly simple test, however, according to *Paper*, and one which may be easily carried out by the average dyer, is the following:—A sample of the silk to be tested is placed in a small porcelain dish and concentrated sulphuric acid is poured over the fibres. If the sample consists of collodion silk no coloration appears until about an hour has elapsed, when the acid solution will acquire a pale yellow colour.

In the case of cuprate silk the acid becomes yellow immediately, and the colour becomes deeper on standing. In the case of viscose silk the acid immediately develops a reddish brown colour, deepening to a rusty brown after standing for an hour.—*Chemical Engineer*, xvi., No. 5.

Royal Institution.—A General Meeting of the Members of the Royal Institution was held on the 5th inst., the Duke of Northumberland, President, in the Chair. Mr. Milner Brown, Dr. H. Wildon Carr, Mr. Emile Garcke, Mr. J. Currie Hanson, Mr. H. Holloway, J.P., Dr. R. Lessing, and the Duke of Rutland, were elected Members. The Secretary announced that His Grace the President had nominated the following gentlemen as Vice-Presidents for the ensuing year:—Dr. Henry E. Armstrong, the Right Hon. A. J. Balfour, J. H. Balfour Browne, Sir William Crookes, Dr. Donald W. C. Hood, the Right Hon Sir James Stirling, Sir James Crichton-Browne (Treasurer), and Alexander Siemens (Secretary).

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, April 24th, 1913.

Sir ARCHIBALD GEIKIE, K.C.B., President, fn the Chair.

PAPERS were read as follows :—

"*Protostigmata in Ascidians.*" By A. G. HUNTSMAN.

"*Origin of the Ascidian Mouth.*" By A. G. HUNTSMAN.

"*Experiments on the Kidneys of the Frog.*" By F. A. BAINBRIDGE, S. H. COLLINS, and J. A. MENZIES.

"*Probable Value to* Bacillus coli *of* '*Slime.*' *Formation in Soils.*" By CECIL REVIS.

When kept in sterilised soils, particularly if these contain excreta, *B. coli* shows a great tendency to the formation of "slime," a property which is retained for some time when the organism is plated out on ordinary nutrient media. It has been found that soils so inoculated with *B. coli*, together with other soil organisms of a sporogenous type, are able to retain and absorb moisture from the air in a remarkable manner, so that during a period of three years flasks containing these soils and only closed with cotton-wool plugs retained and even increased the original water added to them, whilst controls which did not contain the *colon* organism rapidly dried up. This property is attributed to the "slime" produced by *B. coli*.

"*Variation in* Bacillus coli. *Production of Two Permanent Varieties from One Original Strain by means of Brilliant Green.*" By CECIL REVIS.

The effect of growth in ordinary broth containing brilliant green on the physiological activity of organisms of the *colon* group has been studied. Whilst in all cases considerable modification in physiological activity was observed, in this particular case two organisms were obtained from the original culture (itself obtained from a single cell) one of which showed marked resistance to the dye stuff, whilst the other underwent profound and increasing modification, finally completely losing certain of its original fermentative powers. Both types so obtained were permanent in themselves and different to the original culture.

From these experiments it appears—

1. That from one single cell there may arise new cells differing in the power of resistance to the same environment and consequently modified by it in a different manner.
2. That the exhibition of physiological activity is not an intrinsic and integral part of the protoplasm, but that such powers may be entirely lost without loss of vitality in the organism itself.

CHEMICAL SOCIETY.

Ordinary Meeting, April 3rd, 1913.

Prof. W. H. PERKIN, LL.D., F.R.S., President, in the Chair.

(Concluded from p. 214).

92. "*The Influence of Colloids and Fine Suspensions on the Solubility of Gases in Water.* Part III. *Solubility of Carbon Dioxide at Pressures Lower than Atmospheric.*" By ALEXANDER FINDLAY and THOMAS WILLIAMS.

The solubility of carbon dioxide in solutions of ferric hydroxide, dextrin, starch, gelatin, egg-albumen, and silicic acid, and in presence of suspensions of silica and of charcoal, has been determined at 25° for the range of pressure from 250 mm. to 760 mm. of mercury. General confirmation of Findlay and Creighton's results (*Trans.*, 1910, xcvii., 536) has been obtained, and it was also shown that the solubility of carbon dioxide in colloidal solutions is relatively high at low pressures, and that it diminishes with increasing pressure either to a constant value, or to a minimum value, after which the solubility increases again with rising pressure.

93. "*Quinonoid Addition as the Mechanism of Dye-stuff Formation.*" By ARTHUR GEORGE GREEN.

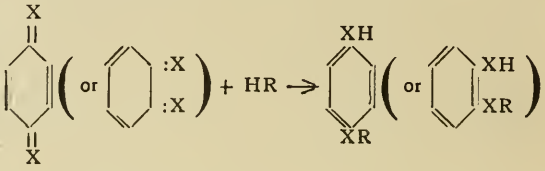
The following generalisation correlates a large number of well known facts, and affords a ready explanation of the ease with which many very complex dye-stuffs are produced.

1. All quinones and quinone-like compounds, by reason of their high degree of "unsaturation," exhibit a great attraction for hydrogen or equivalent groups by the assumption of which they can pass into more saturated compounds.

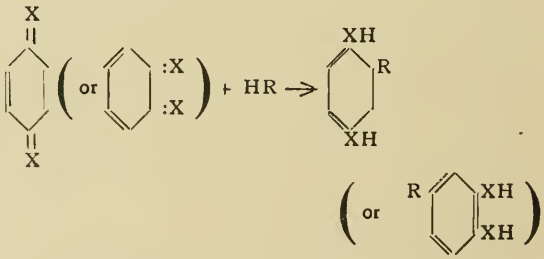
2. A very large proportion of dye-stuff syntheses and the individual steps in such syntheses may be represented as consisting in the linking up of molecules brought about through the attractive forces of quinonoid groups.

3. Such reactions may occur in two ways, namely :—

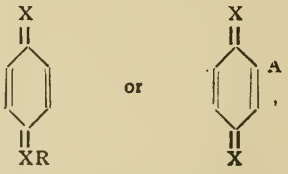
(*a*) *Direct Addition* :—



(*b*) *Indirect Additions* :—



4. In the presence of an oxidising agent, such as chromic acid, atmospheric oxygen, nitrobenzene, or another quinonoid compound, the above additive products may be again converted into quinonoid derivatives,—



which under suitable conditions are ready to react again in the same way as before. Such alternate additions and re-oxidisations may occur several times in succession, thus producing very complex molecular structures, such as those in the induline and aniline-black series.

94. "*Sodium Iodide with Acetone of Crystallisation.*" By KATHLEEN SHIPSEY and EMIL ALPHONSE WERNER.

When anhydrous sodium iodide is dissolved in warm acetone, the solution on cooling, and after remaining for a short time, furnishes large glassy elongated prisms, which have the composition $NaI,3C_3H_6O$. The crystals effloresce immediately after removal from the solution, and rapidly lose all the acetone on exposure to the air. A specimen of the crystals rapidly drained off from the mother liquor gave the following results :—

Loss on exposure to dry air = 55·2. Found, I = 38·91. $NaI.3C_3H_6O$ requires C_3H_6O = 53·7; I = 39 19 per cent.

When ordinary acetone (b. p. 56—57°), is used, the crystals that are deposited have a brownish pink colour, which is only partly due to free iodine, only a very faint colour being produced with a fresh starch solution.

From pure acetone the compound separates in colourless crystals, which assume a pale yellowish brown colour after remaining in the liquid for twenty-four hours. The existence of this compound was noticed during the employment of a solution of sodium iodide in acetone for the preparation of certain iodo-derivatives.

Quite recently Marsh and Rhymes (*Proc.*, 1913, xxix., 62) have described some double salts containing the iodides of potassium, ammonium, rubidium, and lithium with acetone of crystallisation, but curiously enough, no compound containing sodium iodide is referred to, whilst neither potassium nor ammonium iodides have yielded a compound under the same simple conditions as the sodium salt.

No compound was obtained when sodium iodide was dissolved in methyl ethyl ketone, acetylacetone, or ethyl acetoacetate.

A preliminary experiment has shown that when the compound $NaI,3C_3H_6O$, prepared from commercial acetone, is heated on the water-bath, it gives a distillate of acetone which is devoid of any reducing action on a solution of potassium permanganate. The preparation of chemically pure acetone in a simple manner by the aid of this compound is being examined.

95. "*Denitrification the Result of Enzyme Action.*" (Preliminary Note). By William Hulme.

A fluorescent, denitrifying organism, from contact-bed slurry, was grown in nitrate-broth, and after several days the whole was filtered through a Chamberland filter into a sterilised bottle. This filtrate, the sterility of which was checked by plate culture, was then tested for enzyme action as follows :—

Three tubes, containing equal quantities of sterile nitrate-broth, were treated with equal quantities of the above filtrate (containing nitrite) and respectively (*a*) left untreated, (*b*) boiled, (*c*) treated with toluene. After remaining at 37° for some hours, the ratio of nitrite present was found to be $a : b : c = 2 : 1 : 2$.

The action of the "enzyme" free from nitrite was then investigated. Nitrate-broth was inoculated, and, after some days, was filtered through a Chamberland filter, as above. The filtrate was then precipitated with an excess of absolute alcohol and sodium chloride, the precipitate washed with absolute alcohol, and finally dissolved in distilled water. Equal quantities of this solution were added to 1 per cent potassium nitrate solution, and the resulting nitrite production, after some hours, was as follows :—

(*a*) 1 per cent potassium nitrate solution alone	No nitrite
(*b*) Enzyme solution alone	No nitrite
(*c*) 1 per cent potassium nitrate solution + enzyme solution	Very strong
(*d*) 1 per cent potassium nitrate solution + enzyme solution (boiled)	Strong

These results seem to show that denitrification is the result of enzyme action, and the whole question is now undergoing complete investigation.

96. "*Allylamine Derivatives: the Identification of Proline.*" By Wilhelm Gluud.

Some derivatives of allylamine have been studied as to their capacity of yielding pyrrole compounds. Oxalylmonoallylamine proved to be a good material for this purpose, readily furnishing oily products containing pyrrole compounds. It was prepared from ethyl oxalate and hydrolysis of the ester thus obtained, the interaction of oxalic acid and allylthiocarbimide not giving a sufficient yield of oxalylmonoallylamine.

Allylglycine was prepared from chloroacetamide and allylamine, and the allylamine hydrochloride removed with baryta and lead oxide. The copper salt was prepared in order to find out whether it can easily be distinguished from the corresponding salt of proline having the same empirical formula. It was found to be very similar to the copper salt of proline, but, unlike the latter, is anhydrous, so that the usual method of identifying the proline salt by estimation of water and copper is sufficient to distinguish it from the copper salt of allylglycine.

97. "*Solubilities of Salts of Ammonium Bases in Water and in Chloroform. Part I. Solubility as a Constitutive Property.*" By Cyril James Peddle and William Ernest Stephen Turner.

With the object of testing whether any relationships exist betwen chemical composition and solubility, and between solubility and other physical properties, determinations have been made at the common temperature of 25° of the solubilities of twenty-four salts of ammonium bases in water, and of twenty-two of them in chloroform. The salts included chlorides, bromides, and iodides derived from amines related in such a way as to make a comparison possible, both of homologues and of isomeric substances; whilst the two solvents were of quite different types, the one an ionising, the other a neutral, medium.

It was shown that the substitution of organic radicles for hydrogen in an ammonium salt increases the solubility both in water and in chloroform, the increase being very great for alkyl radicles, but much smaller for aromatic. Chloroform was found an exceptionally good solvent for these salts.

On the whole, solubility in water decreases with increase in the mass of the substance; in chloroform, on the other hand, it increases. It was further shown that beyond a probable additive relationship between the solubilities in water of salts derived from the amines, the property is a highly characteristic one.

The effect of the relative molecular states of solvent and solute, as also of their respective dielectric constants, was also discussed.

Ordinary Meeting, April 17th, 1913.

Prof. W. H. Perkin, LL.D., F.R.S., President, in the Chair.

The President referred to the death on March 3 of Mr. Frank Standish Findon, who was elected a Fellow on May 4, 1905.

It was annonnced :—

1. That the van't Hoff Memorial Lecture will be delivered by Prof. James Walker, F.R.S., on Thursday, May 22, 1913, at 8.30 p.m.

2. That the Council has appointed the following Committees for the year 1913-14 :—

Finance Committee—Messrs. E. G. Hooper, G. T. Moody, Sir Edward Thorpe, Sir William Tilden, and the Officers.

House Committee—Messrs. Horace T. Brown, W. R. Dunstan, R. Messel, J. E. Reynolds, J. M. Thomson, Sir Edward Thorpe, Sir William Tilden, and the Officers.

Library Committee—Messrs. B. Dyer, W. Gowland, A. Harden, J. T. Hewitt, C. A. Keane, A. R. Ling, T. M. Lowry, R. Meldola, E. J. Mills, J. M. Thomson (chairman), Sir William Tilden, J. A. Voelcker, the Editor, and the Officers.

Publication Committee—Messrs. H. B. Baker, J. N. Collie, F. G. Donnan, B. Dyer, M. O. Forster, T. M. Lowry, A. McKenzie, F. B. Power, and the Officers.

Research Fund Committee—Messrs. H. B. Baker, W. R. Bousfield, Horace T. Brown, J. N. Collie, H. B. Dixon, J. J. Dobbie, M. O. Forster, P. F. Frankland, A. Liversidge, W. J. Pope, and the Officers.

Messrs. R. B. Bourdillon, Thomas J. Kirkland, J. E. Barbary, E. K. Rideal, J. W. Smith, V. Steele, and C. E. Cooke were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. William Love Biggart, Rossarden, Kilmalcolm, Renfrewshire; Ghulam Ali Mahamadi, B.A., Elliehpur, Berar, India; Ralph Richard Oliver, care of Messrs. The Southern Fibre Co., Portsmouth, Va., U.S.A.; Ernest John Wilson, M.A., Osborne House, Wisbech.

Certificates have been authorised by the Council for presentation to ballot under By-law I. (3) in favour of Messrs. Hilton Ira Jones, Dakota Wesleyan University, Dakota, U.S.A.; Kali Prosonuo Rai, 147, Baranoshee Ghose Street, Calcutta; Cornelius Williams, School of Agriculture, Cedara, Natal, South Africa.

Of the following papers, those marked * were read:—

*98. "*The Action of Tartaric Acid on Tin in the Presence of Oxygen.*" By ALFRED CHASTON CHAPMAN.

When tin is partly immersed in a 5 per cent aqueous solution of tartaric acid, no action occurs unless air is present. In these circumstances oxidation takes place at the surface of the liquid, and stannous tartrate is formed. If the action is allowed to proceed at the ordinary temperature, well-formed crystals slowly separate, the solutions in the case of the author's experiments having been allowed to remain undisturbed for three years. Contrary to existing statements, stannous tartrate readily undergoes dissociation even in the presence of tartaric acid, yielding under some conditions a colloidal solution. In the presence of a restricted supply of oxygen the stannous oxide undergoes slow oxidation, forming a brown coloured colloidal solution, which may contain as much as 6 per cent of tin, and which, when heated with free exposure to the air, becomes converted into a bluish white colloidal liquid containing hydrated stannic oxide. The brown coloured solution evidently contains an oxide of tin intermediate between stannous and stannic oxides—probably the sesquioxide, the existence of which on theoretical grounds is very probable, and which has been referred to by several observers. That the oxide in question is not a molecular compound of stannous and stannic oxides is rendered probable by the fact that the brown colour is developed in solutions containing as much as 20 per cent of sulphuric acid. Attempts to isolate the intermediate oxide and to prepare a tin alum have not been successful up to the present.

DISCUSSION.

Mr. F. P. WORLEY asked if the author had thought of employing other oxidising agents, such as hydrogen peroxide, in place of atmospheric oxygen. The latter obviously acted as depolariser, uniting with the hydrogen of the acid to form water, thus supplying sufficient energy to make the interaction exothermic.

Mr. CHAPMAN said that the conditions under which the coloured oxide was formed, and the fact that similarly coloured solutions could be obtained in the presence of 20 per cent sulphuric acid, rendered it, in his opinion, exceedingly probable that the oxide was a definite oxide—probably the sesquioxide—and not a combination of two oxides. The precise causes leading to the formation of the colloidal condition were often very difficult to determine, and he had not been able to ascertain why the stannous hydroxide assumed a colloidal state in some cases and not in others. The crystals formed in these experiments consisted of pure stannous tartrate, and there was no evidence that the OH-groups had been attacked. The effect of hydrogen peroxide and permanganate had not been tried. Only two experimental bottles had been kept in the dark, and in neither case had there been any action on the tin, but this might quite well have been due to the fact that in these bottles the corks were air-tight.

*99. "*The Reaction between Ferric Salts and Thiocyanates.*" By JAMES CHARLES PHILIP and ARTHUR BRAMLEY.

It has been observed by various workers that the colour of the red solution obtained by mixing a ferric salt and a thiocyanate gradually diminishes in intensity. This is associated with the progressive reduction of the ferric iron to the ferrous condition, and the present investigation deals with (1) the products of the reaction, (2) the velocity of the reduction, as this is affected by altering the concentration, temperature, and other factors.

Corresponding with the reduction of the iron, there is an oxidation of thiocyanic acid, the sulphur appearing as sulphuric acid and the carbon as carbon dioxide, whilst the nitrogen of the oxidised acid is converted, partly at least, into ammonia.

The velocity of reduction of the ferric iron is quite appreciable at the ordinary temperature, and increases rapidly as the temperature rises. At a given temperature the change is very much slower when ferric salt is in excess than when thiocyanate is in excess. In the latter case addition of acid retards the reaction to a notable extent.

*100. "*The Preparation of Pure Bromine.*" By ALEXANDER SCOTT.

The author recommends as the source of the purest bromine commercial potassium bromide, which has been boiled with small quantities of bromine water in order to eliminate any trace of iodine which may be present. The bromide, after recovery from the solution, should be fused with potassium dichromate in quantity somewhat less than that required for the liberation of all the bromine on treatment with sulphuric acid. The bromine thus obtained is free from chlorine, iodine, and all organic compounds.

The bromine of commerce may be completely freed from the other halogens by shaking it with small quantities of pure sodium hydroxide solution, when the chlorine is removed as chloride and the iodine as iodate.

It is easy to detect 1 part of iodine in 100,000 of bromine in this way by means of nitrosulphonic acid and chloroform, using only 10 cc. of bromine.

A simple form of apparatus, entirely of glass, was shown for the distillation of large quantities of bromine and similar substances without any inconvenience.

*101. "*The Preparation of Conductivity Water.*" By ROBERT BOURDILLON.

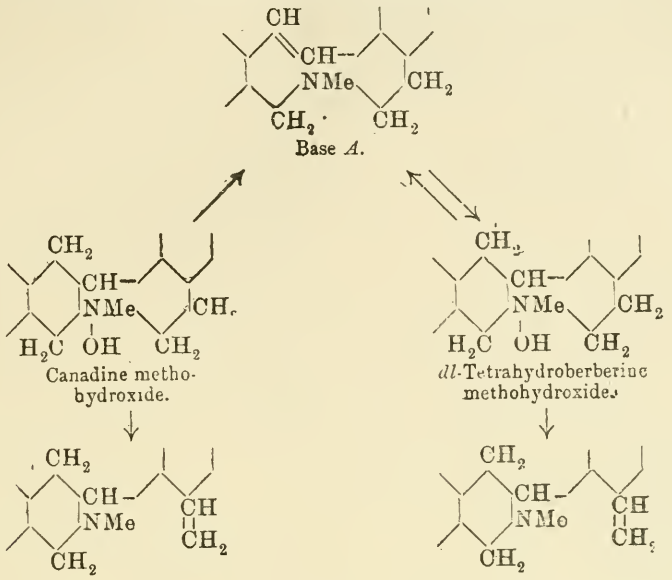
Most of the methods hitherto described for preparing conductivity water produce water of a conductivity of 0·7 gemmho or more. A still has been made which gives 7 or 8 litres of water of a conductivity below 0·2 gemmho by a single distillation from tap water. The essential features are a large copper boiler, a spray trap consisting of a spiral coil of copper tubing, a condenser made of a vertical tin tube up which a current of purified air is passed, and the addition of a little potassium hydrogen sulphate to the water in the boiler. It is also found that by the use of an air-tight electrolytic cell, water of a conductivity of less than 0·2 gemmho can be kept with only a very slow rise of conductivity, so that very dilute solutions can be studied accurately.

DISCUSSION.

Mr. BOURDILLON said, in reply to Prof. Baker, that the copper coil and trap described were loosely jacketed with cotton waste and boiler felt, but, in spite of this protection, about one-sixth of the steam from the boiler was condensed there.

*102. "*The Constitution of the Anhydro-bases Derived from Tetrahydroberberine Alkyl Hydroxides.*" By FRANK LEE PYMAN.

The formation of anhydro-bases by the dehydration of tetrahydroberberine and *l*-canadine (*l*-tetrahydroberberine) methohydroxides has been investigated. It was shown that in the former case two, and in the latter three, isomeric anhydro-bases are formed. As a result of the experimental data and theoretical considerations, it was concluded that the formation of the anhydro-bases may be explained by the following scheme:—



The views of Voss and Gadamer (*Arch. Pharm.*, 1910, ccxlviii., 43) and of McDavid, Perkin, and Robinson (*Trans.*, 1912, ci., 1208) with regard to the constitution of the anhydro-bases derived from tetrahydroberberine alkyl hydroxides were discussed.

103. "*The Application of Hofmann's Reaction to Dialkylacetamides.*" By FRANK LEE PYMAN.

It was shown that the dialkylacetamides—in particular dipropylacetamide—do not behave precisely similarly to the normal aliphatic acid amides (compare Hofmann, *Ber.*, 1882, xv., 407, 752, 762; 1884, xvii., 1406, 1920) in respect of their behaviour to bromine and alkali.

Thus *diethyl-* and *dipropyl-acetobromoamides* are readily obtained in a crystalline form, whilst the bromoamides of the acids of the normal aliphatic series higher than propionic acid cannot be so isolated.

Dipropylacetobromoamide when treated with an excess of aqueous sodium hydroxide gives δ-aminoheptane in a yield amounting to 84 per cent of the theoretical, whilst its isomeride, *n*-octoamide, under similar conditions yields only 30 per cent of the theoretical quantity of *n*-heptylamine.

Normal aliphatic acid amides (2 mols.) when treated with bromine (1 mol.) and aqueous alkali hydroxides give acylalkylcarbamides in excellent yield—

$$2R\cdot CO\cdot NH_2 + Br_2 + 2KOH = R\cdot CO\cdot NH\cdot CO\cdot NH\cdot R + 2KBr + 2H_2O,$$

but the dialkylacetamides, higher than *iso*butyramide, yield little or no acylalkylcarbamide, the corresponding dialkylcarbamide, for instance, s-*di*-δ-*heptylcarbamide* in the case of dipropylacetamide, being obtained.

The behaviour of dialkylacetamides thus resembles more closely that of phenylcarbimide than that of the normal aliphatic acid amides.

104. "*Derivatives of* o-*Xylene.*" By JOHN LIONEL SIMONSEN.

A full account was given of work which has already been briefly mentioned (*Proc.*, 1913, xxix., 26). The following substances were described:—3-*Nitro*-o-*xylene*-5-*sulphonic acid*, 3-o-*xylidine*-5-*sulphonic acid*, 3-*nitro*-o-*xylene*-4-*sulphonic acid*, 3-o *xylidine*-4 *sulphonic acid*, 4-*nitro*-o-*xylene*-5-*sulphonic acid*, 4-o-*xylidine*-5-*sulphonic acid*, 3-o-*xylidine*-6-*sulphonic acid*, and 4-o-xylidine-6-sulphonic acid.

105. "*Synthetical Production of Derivatives of Dinaphthanthracene.*" By WILLIAM HOBSON MILLS and MILDRED MILLS.

In connection with their recent communication on this subject (*Trans.*, 1912, ci., 2194) the authors overlooked a paper by Dr. Ernst Philippi, "Ueber eine Synthese von Linearen Diphthaloylbenzol" (*Monatsh.*, 1911, xxxii., 631), in which is described the preparation of dibenzoyl*iso*phthalic acid, dibenzoylterephthalic acid, and dinaphthanthradiquinone by the same methods as were employed by them. The authors greatly regret their oversight.

106. "*The Alcohols of the Hydroaromatic and Terpene Series.*" (Preliminary Note). By ROBERT HOWSON PICKARD, WILLIAM LEWCOCK, and JOSEPH YATES.

The methods adopted for the isolation and purification of the borneols and *iso*borneols (*Trans.*, 1907, xci., 1973) and of the menthols (*Trans.*, 1912, xi., 109) have been applied to fenchyl alcohol and *iso*pulegol.

The reduction of *d*-fenchone by means of sodium in moist ethereal solution yields *l*-fenchyl alcohol, very little (if any) of the other possible isomeride being formed. This alcohol, by purification of the hydrogen phthalate, has now been obtained with a higher rotatory power than that stated in the literature. The successive fractionations of the magnesium and cinchonine (m. p. 174°) salts of this ester yield a *hydrogen phthalate* (m. p. 147° with $[\alpha]_D$ +22·4° in chloroform), which, when hydrolysed, gives *l*-fenchyl alcohol with $[\alpha]_D$ 20 −15·5°.

Tiemann (*Ber.*, 1896, xxix., 914) prepared *iso*pulegol with $[\alpha]_D$ −2·9° from the condensation products of citronellaldehyde. His work has been repeated, and from these products one of the theoretically possible *iso*pulegols has been isolated in a pure state. This has a specific rotatory power $[\alpha]_D$ 20° −22·2°, and forms a *hydrogen phthalate*, which melts at 106°, has $[\alpha]_D$ −18·7° in chloroform, and forms a *magnesium* salt, melting at 115° with $[\alpha]_D$ +14·1° in ethyl acohol, and a *strychnine* salt, melting at 205° with $[\alpha]_D$ −17·1 in chloroform.

The application of these methods to the isolation in a pure state of the tertiary alcohols has been hindered by the difficulty of preparing their acid esters. The interaction at, say, 110° or above of equivalent amounts of such alcohols and acid anhydrides (phthalic, succinic, or camphoric) leads to the dehydration of the alcohols. It has, however, now been found that the long-continued action at temperatures below 100° of the anhydrides on an excess

of the alcohols gives good yields of the desired acid esters. In this manner optically inactive terpineol has been converted into its esters. The *hydrogen phthalate* melts at 117° and the *hydrogen succinate* at 45°, whilst both esters form crystalline salts with the commoner alkaloids.

(To be continued).

ROYAL INSTITUTION.

Annual Meeting, May 1st, 1913.

Sir JAMES CRICHTON-BROWNE, Treasurer and Vice-President, in the Chair.

THE Annual Report of the Committee of Visitors for the year 1912, testifying to the continued prosperity and efficient management of the Institution, was read and adopted. Thirty-nine new members were elected in 1912. Sixty-three Lectures and twenty Evening Discourses were delivered in 1912. The books and pamphlets presented amounted to about 242 volumes, making with 737 volumes (including periodicals bound) purchased by the Managers, a total of 979 volumes added to the Library in the year.

Thanks were voted to the President, Treasurer, and Secretary, to the Committees of Managers and Visitors, and to the Professors, for their valuable services to the Institution during the past year.

The following gentlemen were unanimously elected as Offices for the ensuing year:—

President—The Duke of Northumberland.

Treasurer—Sir James Crichton-Browne.

Secretary—Alexander Siemens, Esq.

Managers—Dr. Henry E. Armstrong; the Right Hon. Arthur J. Balfour; the Right Hon. Lord Blyth; J. H. Balfour Browne; Dr. Horace T. Browne; the Right Hon. Sir Ernest Cassel; Sir William Crookes; Dr. Donald W. C. Hood; Sir John Jackson; Sir Alexander Mackenzie; Sir Alfred Mond, Bart.; Edward Pollock; Edward B. Poulton; the Right Hon. Sir James Stirling; and Alan A. Campbell Swinton.

Visitors — Dugald Clerk; Alexander Goschen; Dr. William J. Gow; Robert K. Gray; William A. T. Hallowes; Dr. Arthur Croft Hill; James Y. Johnson; G. Lawson Johnston; H. R. Kempe; A. H. Savage Landor; Carl E. Melchers; Charles E. S. Phillips; Dr. W. N. Shaw; Harold Swithinbank; and Arthur J. Walter.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Academie des Sciences. Vol. clvi., No. 8, February 24, 1913.

Fusibility of Natural Fats.—H. Le Chatelier and Mdlle. Cavaignac.—The authors' experiments show that the fusion of fats, like that of all other substances, is a reversible phenomenon. The exact temperature of the transformation can be determined without difficulty to within one-tenth of a degree, although the experiments take rather a long time to perform.

Effect of Heating Calcium Carbide.—E. Briner and A. Kuhne.—It is known that if calcium carbide is heated to 800—1000° in a closed vessel it undergoes a remarkable transformation, carbon being liberated. The authors have investigated the phenomenon, and find that the transformation is a simple decomposition of the substance into its elements. The calcium formed is partly evaporated (and can be detected as a sublimate in the cooler parts of the heated tube), and some of it attacks the material of the tube or vessel in which it is heated.

Oxidation of Complex Cobalt-organic Compounds.—H. Colin and A. Sénéchal.—With excess of alkali the salts of cobalt give complex compounds with polyatomic alcohols, acid alcohols, sugars, and all substances containing alcoholic hydroxyls. These compounds are stable only in solution. The cobaltoglyceric, mannitic, and erythritic compounds oxidise rapidly in air, the lactic, malic, and tartaric compounds with more difficulty, while the citric compound is oxidised only by the action of hydrogen peroxide. Thus the tendency towards oxidation seems to depend upon the number and nature of OH groups in the organic molecule. In all cases oxidation gives green solutions which decompose spontaneously giving sesquioxide, or else are reduced, the organic matter being oxidised. The cobaltoglyceric and cobaltolactic compounds are, however, very stable. If the concentration of the soda in the liquid is sufficient to make the complex stable the quantity of oxygen absorbed tends towards a limit, which corresponds to one atom of oxygen to one atom of cobalt. The metal is then in the trivalent state. The oxidation reaction is monomolecular, according to Manchot and Herzog.

MISCELLANEOUS.

Historical Medical Museum.—The Historical Medical Museum, organised by Mr. Henry S. Wellcome, which is to be opened in London towards the end of June next, will include some objects of exceptional historical medical interest. An important exhibit in the science section will be a large collection of the original apparatus used by the famous Galvani in making his first experiments in galvanism in the eighteenth century. A remarkable collection of votive offerings for health will be exhibited. The custom of presenting these offerings in cases of sickness is a very ancient one, and the collection that will be shown is probably the finest ever brought together. It will include Graeco-Roman votive offerings of special anatomical and pathological interest in silver, bronze, marble, and terra cotta, together with a number of similar objects used for the same purpose in medieval and modern times. Ancient microscopes and optical instruments, gathered from all quarters of Europe, will form another important feature, and a selection of surgical instruments used by famous surgeons when operating on historical personages is promised. The collection of amulets and charms connected with English folk medicine will be very complete, and will constitute an exhibit of more than ordinary interest. A fine collection of early medical medals and coins from the Graeco-Roman period, ancient manuscripts, and early printed medical books will also be shown, together with many other objects of interest to medical and scientific men.

NOTES AND QUERIES.

Double Salts.—I should be greatly obliged for information concerning the double salts containing chlorine and fluorine. I have only been able to obtain very meagre information so far, after a long search. —ENQUIRER.

MEETINGS FOR THE WEEK.

TUESDAY, 13th.—Royal Institution, 3. "Recent Physiological Inquiries—Ductless Glands and their Dominating Influence," by Prof. W. Stirling, M.D., &c.

THURSDAY, 15th.—Royal Institution, 3. "Florentine Tragedies—The Burning of Savonarola," by E. Armstrong, M.A.

— Chemical, 8.30. "Studies of Dynamic Isomerism—Part XV., The Influence of Light on Isomeric Change," by T. M. Lowry and H. R. Courtman. "Derivatives of *o*-Xylene—Part III., The presence of a Mobile Nitro-group in each of the Two Trinitro-*o*-xylenes," by A. W. Crossley and W. R. Pratt. "Derivatives of *o*-Xylene—Part IV., Synthesis of 4 : 5-Dibromo-3-*o*-xylenol," by A. W. Crossley and S. Smith. "Synthesis of Unsymmetrical Derivatives of Deoxybenzoin," by J. C. Cain, J. L. Simonsen, and C. Smith.

FRIDAY, 16th.—Royal Institution, 9. "The Pygmies of New Guinea," by Capt. Cecil G. Rawling.

SATURDAY, 17th.—Royal Institution, 3. "Humphrey Internal Combustion Pumps," by H. A. Humphrey, M.Inst.C.E.

THE CHEMICAL NEWS.

Vol. CVII., No. 2790.

THE MINERALOGICAL ANALYSIS OF SOILS.*

By WILLIAM H. FRY.

Soil may be considered as a mixture of solid, liquid, and gaseous matter. The solid matter consists of mineral and organic material which react with each other and with the liquid and gaseous material. By far the larger part of the solids, the *débris* of rocks, is a mixture of minerals. These minerals comprising the greater part of the soil furnish part of the so-called plant food to vegetation through the medium of the soil solution, and is the chief factor influencing the texture of the soil. Much chemical work has been done upon the soil; but experience has shown that chemical analyses throw very little light upon many soil problems. So far, very little work of a purely mineralogical character has been done in connection with these problems, especially in America. This is rather surprising considering the importance of an accurate knowledge of all soil constituents and the recent high development of petrographic methods. Work has been undertaken by the Bureau of Soils which, it is hoped, will put the subject of soil mineralogy upon a firm basis and create interest in a subject which cannot fail to be of great value to both the farmer and the scientist engaged with agricultural problems.

Certain generalisations concerning the component soil minerals have been established. Thus, chemical analyses have proven that the larger part of the potash and phosphatic material is concentrated in the finer mechanical separates of the soil (G. H. Failyer, J. G. Smith, and H. R. Wade, "The Mineral Composition of Soil Particles," *Bull.* 54, Bureau of Soils, U.S. Department of Agriculture). The most far-reaching and important generalisation yet reached is that "practically every soil contains all the common rock-forming minerals" (F. K. Cameron and J. M. Bell, "Mineral Constituents of the Soil Solution," *Bull.* 30, Bureau of Soils, U.S. Department of Agriculture; F. K. Cameron, "The Soil Solution," 1911; "An Introduction to the Study of the Soil Solution," *Journ. Phys. Chem.*, 1910, xiv., 320).

Of course the relative proportions of soil minerals may and do vary widely. But the number of minerals that can be found in even an apparently pure quartzose beach sand is often quite large. The extreme mineralogical heterogeneity of soils is not surprising, when their origin and the various processes, both physical and chemical, to which they are subjected are considered. All rocks, while they may consist essentially of only a few minerals, do, in reality, contain a large number of species when sufficiently large masses of the rock are considered. In the processes of weathering the rarer mineral species are concentrated. The various weathering processes alter certain minerals, thus giving rise to other species. Wind and water, by their transporting and mixing action, add many minerals to soils (E. E. Free, "The Movement of Soil Material by the Wind, with a Bibliography of Eolian Geology," by S. C. Stunz and E. E. Free, *Bull.* 68, Bureau of Soils, U.S. Department of Agriculture, 1910). Thus the mineral heterogeneity of soils is being constantly maintained.

In order to make a mineralogical analysis of a soil, certain preliminaries are often necessary and always advisable. Quartz constitutes by far the predominant part of practically all soils, and it is often convenient to eliminate this mineral from the sample in order to decrease the time which would otherwise be consumed in locating the various minerals to be determined. This elimination can be easily accomplished by means of heavy solutions, such as methylene iodide or Thoulet's solution in connection with an Harada separator or other specially constructed tubes. Minerals containing magnetic elements, as iron, can be eliminated by means of an electro-magnet. The portions from these separations will be found to lend themselves much more readily to a rapid mineralogical analysis than do the unseparated soils. In order to separate the component minerals according to size of grain, a series of sieves supplemented by the method of centrifugal mechanical analysis is used (Lyman J. Briggs, F. O. Martin, and J. K. Pearce, "The Centrifugal Method of Mechanical Soil Analysis," *Bull.* 24, Bureau of Soils, U.S. Department of Agriculture). By this method the soil is separated into various portions, the diameters of the grains of each portion being constant within quite narrow limits. This separation according to size is necessary when quantitative results are required. Various microchemical tests may be used in the determination of many of the minerals, and direct chemical tests upon the soil will often aid in the detection of the presence or absence of certain groups of minerals, such, for example, as the sulphates or chlorides.

For the determination of the optical constants of the minerals, a petrographic microscope is desirable. But any microscope which can be adjusted with a condensing lens, nicol prisms, both analyser and polariser, a rotating stage, and an eye piece with cross hairs, can be used.

After the material has been prepared for the examination, a small quantity is transferred to a microscopic slide. The material is then embedded in an oil of a definite refractive index. A series of oils with definite refractive indices are kept for this purpose. An oil having an index nearly equal to that of quartz serves best as a general embedding medium. The preparation is now covered with a cover glass and is ready for examination. The refractive index of any particular grain can be determined by comparison with the oil in which it is embedded. Should the indices of the mineral be either higher or lower than that of the oil, the grain will stand out with a noticeable relief. Whether the index of the grain is higher or lower can be determined by means of the Beche lines or by the method of inclined illumination of Schroeder van der Kolk. (A detailed account of all methods used in microscopic soil mineralogy will be found in a forthcoming bulletin of this Bureau; "The Microscopic Determination of Soil-forming Minerals," by W. J. McCaughey and W. H. Fry). Various oils may be used until one is found with practically the same index of refraction as that of the mineral, or the index may be roughly approximated, after a little practice, by the relief of the mineral.

The index of refraction having been determined, or approximated, the other optical characteristics are determined. By crossing the nicols and rotating the stage, it is immediately determined whether the mineral is isotropic or anisotropic, except in cases of a uniaxial mineral perpendicular to an optic axis, in which case an interference figure can be obtained, since isotropic minerals remain dark during the rotation. Should the mineral be anisotropic, whether it is uniaxial or biaxial, is determined by means of interference figures obtained by crossing the nicols and removing the eye-piece. Uniaxial minerals give a dark cross, biaxial mineral either one or two hyperbolæ according to the optical orientation of the grain. The extinction angle can be measured by aligning a cleavage crack or crystal face of the grain with one of the cross hairs and rotating the stage until the grain becomes dark. The position or negative character of the mineral is obtained with the aid of a quartz or mica wedge or selenite plate. These characters in conjunction with the refractive index and the morphological character of the mineral, cleavage, form, and so forth, are usually sufficient to identify the mineral. Should they not be sufficient, then further optical tests may be applied, such as the measurement of the optic angle, and so on. All of these

* Published by permission of the Secretary of Agriculture, U.S.A. From the *Journal of Industrial and Engineering Chemistry*, v., No. 1.

tests can be performed very quickly. Then another mineral grain in the preparation is selected, and the same procedure applied to it, until all of the grains in the preparation have been determined.

Should quantitative results be desired, they are obtained by the aid of an eye-piece checkerwork micrometer. The minerals in the preparation being known, and all being of practically the same diameter, the percentage of any one or more species of the mineral can be gotten by count in conjunction with the micrometer as an aid and check.

So far, the limitations of the microscope have prevented the examination of the mechanical separates other than the sands and the silts. The clays, on account of the extreme minuteness of the grains, do not lend themselves to a microscopic mineralogical analysis.

A large number of analyses have been made by this laboratory, and will be published in other connections where they will be fully discussed. A few only, taken more or less at random, are given here, to give some idea of the mineral complexity of the soil. Only one quantitative examination is included.

Soil Series.

(Cecil W. J. McCaughey, Analyst).

Minerals other than Quartz.

Sand.	Silt.
3—5 per cent	10 per cent

Abundant and Characteristic Mineral.

Zircon	Sillimanite
Sillimanite	Chlorite
Rutile	Muscovite
Microcline	Orthoclase
Plagioclase	
Biotite	

Less Abundant or Accessory Minerals.

Epidote	Garnet
Muscovite	Hornblende
	Epidote
	Tourmaline

Remarks.—Stretched and undulatory quartzes. Grain mostly subangular.

From this analysis it is seen that quartz constitutes by far the larger percentage of the separates examined. In all, fourteen minerals were determined.

Some qualitative analyses of various soils are as follows.:—

Sierra Sandy Loam from Sacramento Area.—Magnetite, quartz, anorthite, andesine, oligoclase, labradorite, orthoclase, microcline, hornblende, hypersthene, zoisite, muscovite, biotite, tourmaline, epidote, zircon.

Orangeburg Sandy Loam.—Magnetite, quartz, oligoclase, microcline, orthoclase, albite (oligoclase-albite), labradorite, biotite, garnet, zircon, epidote, apatite (enclosed in quartz), muscovite).

This soil seems very low in ferric minerals.

Norfolk Sandy Loam.—Quartz, apatite (enclosed in quartz), rutile (enclosed in quartz), tourmaline, magnetite, albite, hornblende, augite, topaz, biotite, andalusite, olivine.

It will be noticed that orthoclase does not appear in this analysis. However, the mineral has been located in small quantities of other samples of the same soil.

Sample Taken from Bed of Creek, Old Brunswick Cove.—Quartz, magnetite, andesine, labradorite, apatite, hornblende, biotite, muscovite, orthoclase.

These analyses represent the sands and silts. It is extremely probable that the clays contain all of the minerals found in the separates of the larger particles. Attrition would inevitably cause particles of the larger minerals to find their place in the clays. In addition, it is known that the clays contain large amounts of kaolin and erruginous matter. Chemical analyses lead us to believe that the mineralogical composition of the clays is far more complex than that of the sands and silts. Work is now in progress which it is believed will demonstrate this.

The most immediate and obvious results of the mineralogical analysis of a soil is that the method gives a rapid qualitative analysis, far more rapid than the ordinary chemical methods. For instance, only a few moments are necessary to determine whether apatite is present abundantly or otherwise. By making a quantitative examination, an approximate idea can be formed as to the amount in the particular soil under examination. Further, the method shows definitely in what form the chemical elements are combined, a result which a chemical analysis leaves to conjecture or to probability. Something concerning the origin of the soil can be learned by the method. If, for example, a soil should contain large quantities of ferro-magnesian minerals, it undoubtedly was derived largely from some basic crystalline rock, which particular rock would of course depend on the mineral species present taken in conjunction with other predominant minerals of the soil. Results have already thrown some light on soil fertility and considerable on ground rock fertiliser problems (see a forthcoming *Bulletin* of this Bureau, "Ground Rock and Ground Minerals as Fertilisers," by W. O. Robinson and W. H. Fry). It is possible that the method may be the means of constructing a mineralogical classification of soils.

IRIDOSMINE FROM THE NEW RIETFONTEIN MINES:

Its Occurrence, Analysis, and Genesis.*

By C. BARING HORWOOD, B.Sc (Lond.), A.R.S.M., A.M.I.C.E.

Introduction.

Iridosmine has been described as an alloy of iridium and osmium in variable proportions (see Note 1). Probably a better definition would be that it consists of an intimate mixture of the two, which generally contains some ruthenium and sometimes a little platinum, chromium, gold, and palladium (Note 2). Such a mixture is generally accompanied by one or more of the less rare elements as impurities, which may be removed by treatment with aqua regia (Note 3).

Occurrence.

Several years ago Mr. Andrew F. Cross (personally communicated) discovered platinum and iridosmine (more often the latter), in the Rand bankets. He first noticed it associated with the gold at the Modderfontein mine, and afterwards at the East Rand Proprietary mines. At the latter he found as high a percentage as 10 dwts. per ton of iridosmine, in the black sands from the stamp batteries. He has also seen it associated with the Black Reef at Klerksdorp (see Note 4).

Quite recently he found as much as 9 dwts. per ton in battery concentrates (black sands) from a Klerksdorp property. Years ago he found it in the banket reef, which immediately underlies the diabase, at the Steyn's Estate mine.

Traces of metals of the platinum group have also been found associated with the gold at the Randfontein mines.

The first to actually publish an account of such an occurrence on the Rand was Prof. R. B. Young ("Notes on the Auriferous Conglomerates of the Witwatersrand," *Trans. Geol. Soc. S.A.*, 1907, x.). He mentioned it as being obtained from the crushed ore of the Du Preez series at the New Rietfontein mines in quantities too small to be of commercial value, and described it as probably an original constituent of the banket, occurring in rounded and flattened grains and in tabular six-sided rhombohedral crystals, both averaging in diameter about 0·12 mm. A very impure sample had a specific gravity of 17·9, and on

* *Transactions of the Geological Society of South Africa*, 1912, xv, 52.

treating for osmium he obtained results which showed that this element was present in considerable quantity.

The writer examined, under the microscope, samples from the Rietfontein mines and from the Klerksdorp district, and found that they were decidedly crystalline in character.

Having been technically connected with the Rietfontein gold mines in 1907 and 1908, it seemed to the author worth while to study the occurrence a little more closely. These mines are situated about nine miles to the east of Johannesburg and about four miles north of Germiston. Their underground workings extend for a distance of about one and three-quarter miles in an east and west direction, parallel to the strike of the banket beds.

At that time the percentage of free gold recovered at these mines (that is the gold which can be recovered by amalgamation) was over 60 per cent of the screen value (Note 5). The iridosmine occurs in minute quantities associated with the gold. It has not been recognised *in situ* underground or in hand specimens of the reefs, but in panning rich samples of ore it is sometimes noticed as occurring in small grey particles at the extreme end of the tail of gold, and it was sometimes impossible to thoroughly separate the two in the pan owing to their specific gravities being so nearly alike (Note 6). From the panning of numerous samples it would seem that the iridosmine occurs mostly in what is known as the Carbon Leader, a very narrow banket reef, varying in thickness from a mere streak up to 2 or 3 inches, rich in gold, and in which the gold is invariably associated with carbon (Note 7).

The iridosmine was collected from the battery concentrates, or black sand residues, and die sands. The black sands that were separated from the plate dressings were daily put into the ball mill, and once a month the accumulation from the latter were put into the Berdan pan, where they were treated for about forty-eight hours, and afterwards the iridosmine was separated from these concentrates by panning; being the heaviest metal it remained in the pan until the last. The quantities in which it occurs are too small for it to be of other than scientific interest; thus it took several months to collect even 1000 grains of the mineral.

Analysis.

Towards the end of 1907 the author took a small quantity with him to England (Note 8). This sample had been heated with aqua regia to free it from any impurities such as iron, or amalgam, collected during its treatment in the stamp battery. Dr. W. J. S. Lockyer (with the sanction of the Director, Sir J. Norman Lockyer) was kind enough to have this subjected to a spectroscopic analysis at the Solar Physics Observatory, South Kensington.

Elements.	Remarks.
Ruthenium ..	Lines very strongly shown.
Osmium ..	Lines very strongly shown.
Iridium . ..	Certainly present; but lines not very strong.
Rhodium ..	Probably present, but cannot establish definitely without a spectrum of increased dispersion.
Platinum ..	Possibly trace of some of the strongest lines, but its presence is very doubtful.
Iron	Lines moderately strong. These occur also in the silver poles spectrum, but are stronger in the spectrum of the sample plus silver poles.
Calcium ..	The lines of these two elements are a little stronger in the spectrum of the poles plus sample than in that of the silver poles alone. The elements probably occur in minute quantities.
Aluminium ..	
Chromium ..	Lines fairly well shown.
Titanium ..	Faint traces of strongest lines.
Silicon	
Magnesium .	
Palladium ..	Trace of strongest lines, apparently.

Silver poles were used (Note 9), and the elements found to be represented in the spectrum are given in the above table.

The above elements are arranged in the order of the strength of their lines in the spectrum.

The following forty-four elements were sought, but there was no evidence of their presence:—

Antimony, arsenic, barium, bismuth, cæsium, cadmium, cerium, cobalt, copper, erbium, europium, gadolinium, gallium, holmium, indium, lanthanum, lead, lithium, manganese, mercury, molybdenum, neodymium, nickel, praseodymium, potassium, niobium, radium, rubidium, samarium, scandium, strontium, sodium, thorium, tin, thulium, tungsten, thallium, tantalum, uranium, vanadium, wisconium, yttrium, ytterbium, and zinc.

As previously mentioned, the material had already been heated with aqua regia at the mine laboratory, and this treatment may have eliminated all traces of some of these latter elements, even if originally present.

On the author's return to the Transvaal early in 1908 he sent another sample weighing 910 grains to England. Dr. Lockyer very kindly had a further spectroscopic analysis made from portions of this sample, for which much larger quantities of the material were taken. Silver poles were again used, and the result is shown below:—

Elements.	Remarks.
*Osmium	Lines very strong.
*Ruthenium ..	Lines very strong.
Iron	Lines fairly strong.
Chromium ..	Lines rather weak.
Calcium	Lines rather weak.
Aluminium ..	Lines rather weak.
Strontium ..	Lines rather weak.
Titanium.. ..	Lines rather weak.
Sodium	Lines rather weak.
*Iridium	Lines rather weak.
Mangnesium ..	Lines weak.
Manganese ..	Lines weak.
Vanadium ..	Slightest trace of strongest lines.

In this analysis there was no trace of platinum, potassium, or silicium.

As before, the elements are arranged according to the strength of their lines in the spectrum, and asterisks have been placed against those elements of which the substance is, probably, mainly composed.

This second analysis bears out the main features of the first one. The amount of iron present in each case is probably chiefly due to iron from the stamp shoes and dies of the battery.

From these analyses it would, at first sight, seem that the substance consists principally of osmium and ruthenium with only a little iridium. Iridium lines are, however, generally weak, so that there might be more iridium present than one would infer from the weak lines in the spectrum, and this was subsequently shown to be the case.

Usually the presence of quantities far too small to be detected by the chemist is quickly and easily detected by a spectroscopic examination.

A spectroscopic analysis is especially useful in certain cases, such as this one, in which the presence of rare elements can be detected quickly and with certainty. However, it is well to bear in mind that it is only qualitative; for example, some elements although present in very minute quantities may give strong lines, while others which are present in larger quantities may give quite weak lines. This depends on whether the element is easily vaporised by the heat of the electric arc, or, in other words, is better able to carry the current, in which case the lines will be relatively strong. It approaches a little to quantitative methods in the case of a differential analysis in which the spectrum of a substance containing a known quantity of an element is compared with that of another substance containing an unknown quantity of the same element when some idea of the relative quantity present can be formed.

Through the courtesy of the Transvaal Mines Department and Mr. R. N. Kotzé, the Government Mining Engineer, an official request was forwarded to the Imperial Institute at South Kensington that a quantitative analysis of this concentrate might be made. The director, Prof. Wyndham R. Dunstan, F.R.S., very kindly undertook to have this done, and, the remainder of the sample, after the spectroscopic analysis had been made, was therefore handed over to the Imperial Institute authorities. The following is a quotation from the Director's report:—

"*Description of Sample.*—The sample received at the Imperial Institute weighed about 20 grms. (about 309 grains), and consisted of a dark fine-grained heavy metallic concentrate. It contained globules of mercury which had probably been introduced during its passage over the battery plates in the process of concentration.

"*Results of Examination.*—The mercury originally present in the concentrate was removed by heating the material prior to analysis; the decrease in weight, which was almost entirely due to loss of mercury, amounted to nearly 12 per cent. After removal of the mercury the concentrate had a specific gravity of about 19, and was found to have the following composition:—

	Per cent.
Gold	1·24
Platinum	0·61
Iron (expressed as Fe_2O_3)	1·29
Nickel (expressed as NiO)	0·66
"Osmiridium" (Ir, Os, and allied metals)	95·52

"The osmiridium was found to contain about 45 per cent of iridium.

"The above results indicate that the concentrate consisted essentially of the mineral iridosmine. The gold was amalgamated with the mercury in the material as received; but the platinum was probably in a free state. Some of the iron was also present in a free state, and was most likely derived from the stamp-shoes used in crushing the ore. The remainder of the iron was probably for the most part in combination with the nickel."

He pointed out that the results of a single analysis may be very misleading, as experience had shown that osmiridium varies greatly in composition, even in the case of samples from the same locality, and that a marked instance of this occurs in the case of an already known South African source of supply.

Notes.

1. "Mineralogy," by F. Rutley, 10th Edition, p. 226. "The Data of Geochemistry," by F. W. Clarke, p. 607. "The Geology of Ore Deposits," by Thomas and MacAlister," p. 34.

2. "The History of Chemistry," Ernst von Meyer, 3rd English Edition, p. 433. F. W. Clarke, *loc. cit.*, p. 18. N.B.—Platinum, iridium, osmium, ruthenium, rhodium, and palladium constitute the platinum group of metals.

3. Since iridium and osmium in a fine state of division are themselves somewhat soluble in aqua regia, the mixture should only be treated sufficiently long with this reagent to dissolve out any of the impurities which may be present.

4. While this paper was going to press a letter from Mr. Lewis Watkins appeared in the *South African Mining Journal* for May 25, in which he states that he found metals of the platinum group in tailings from the Ariston Mine at Klerksdorp, in 1888 and 1889.

5. By "screen value" is meant the value of the ore treated as obtained from the sampling and assay of the pulp leaving the battery screens. For the fourteen months ending February, 1908, the average percentage of gold recovered by amalgamation was about 64 per cent of the screen value.

6. The specific gravities, *when pure*, of gold, iridium, and osmium, are 19·3, 22·7, and 22·5 respectively. The two latter generally contain impurities, and so the specific gravities are reduced, and thus more nearly approach that of gold.

7. For a description of the Rietfontein Reefs see "The Mode of Occurrence and Genesis of the Carbon in the Rand Bankets," by C. B. Horwood, *Trans. Geol. Soc. S.A.*, 1910, xiii.

8. The writer wishes to take this opportunity of thanking Prof. Wm. H. Merrett for his kindness in taking charge of the samples and interesting Dr. Wm. J. S. Lockyer in the matter after the author had left for South Africa.

9. The method employed was explained by the author at the meeting.

(To be continued).

REMOVAL OF FUSIONS IN ALKALINE CARBONATES FROM THE CRUCIBLE.

By R. HOWDEN, B.Sc.

If a pinch of powdered potassium nitrate be dropped into the crucible while the fusion is still red-hot and liquid, the evolved gases render the mass porous, and the whole can be removed from the crucible, by simple solution in hot water, in twenty minutes or less. It is well to give the crucible a circular movement so as to mix the nitrate well with the carbonates, and to spread the latter over the sides of the crucible.

Laboratory, Palmer's Shipbuilding and Iron Co., Ltd.,
Jarrow, May 4, 1913.

THE LATEST ACHIEVEMENTS AND PROBLEMS OF THE CHEMICAL INDUSTRY.*

By CARL DUISBERG.

(Continued from p. 223).

Organic Intermediate Products.

The conversion of the aromatic hydrocarbons into intermediate products necessary for the colour industry is almost always carried out by treatment with concentrated sulphuric and nitric acid, and subsequent reduction of the thus obtained nitro-compound by means of metals or metallic oxides and sulphides. In the production of amines, iron is the principal agent of reduction, while zinc and tin are mostly used in the production of azo-compounds. The electrolytic reduction has not proved useful for these processes.

The methods of producing nitro- and amido-compounds have been very little changed as far as chemical operations are concerned, but with the increase of their production their poisonous properties became more and more apparent and forced manufacturers to modify the processes so that they could be carried out in tightly closed vessels in order to protect the life and health of the workmen.

In Germany legislation has been recently enacted, based on the experience of the individual factories, which lays down rules and regulations for strict observance.

Several trinitro-compounds have been shown to be explosives, and, like trinitrotoluene, are now largely employed as substitutes of picric acid in the manufacture of explosives.

The introduction of oxy-groups into the molecule is mostly brought about by melting sulpho acids with alkalis, and, according to more recent methods, with alkaline earth metals, such as calcium and barium hydrates. Since chlorine, produced electrolytically, is obtainable in unlimited quantities, and chemically pure, chlorine substitution derivatives of the hydrocarbons have been employed for all kinds of synthetical purposes. Many of these

* From the *Journal of Industrial and Engineering Chemistry*, iv., No. 10.

chlorine derivatives can not only be converted into oxy-derivatives by melting with alkalis, but, like paranitro-chlorbenzole, they also directly exchange their chlorine for an amide group when treated with ammonia or its derivatives. Colours also often change their shade when a halogen atom is introduced into their molecule and acquire more valuable properties. Chlorine has therefore proved exceedingly useful in the preparation of intermediate products, and will undoubtedly become of still greater service in the future.

In the naphthalene series, the method discovered by Bucherer and Lepetit for the conversion of the hydroxyl group into the amido group and *vice versâ*, employing sulphurous acid esters, has proved of great practical value. Phosgene, too, is to-day being more and more employed. Several decades ago it became an important substance for the production of the urea of paramidobenzolazo-salicylic acid, introduced into the market under the name of "Cottonyellow," as a beautiful yellow cotton colour of great fastness to light. Its principal use, however, was for the manufacture of the bright but fugitive triphenyl-methane colours. It is now especially used to combine 2 molecules of aromatic compounds with free amido groups, thus producing urea derivatives, and if the starting material is an azo colour, the resulting urea derivative is, as a rule, much faster to light than the original colour. Imidazol, thiazol, and azimido compounds of the most varied kinds are also manufactured and converted into azo colours.

In the series of the aldehydes and carboxylic acids there are no epoch-making discoveries to be recorded. Chemists still start from hydrocarbons chlorinated in the side chain or directly oxidise the homologues of benzole. Kolbe's synthesis of salicylic acid, of which large quantities are used in the colour industry, is also applied at an ever-increasing rate for the production of the oxycarboxylic acids. But the direct introduction of the carboxylic group into the benzole molecule, unsubstituted by hydroxyl, is a greatly desired achievement which, however, has not yet been attained. It is also a matter of greatest importance that in substitution reactions of the aromatic nucleus we should be able to vary at will the ratio of the isomers to be formed.

Besides the biochemical production of ethyl alcohol from wood waste and from the waste liquors of the sulphite cellulose industry, I wish to mention the synthesis of organic compounds by the addition of water to acetylene. In this manner we produce in a simple way acetaldehyde, which can be easily converted into acetic acid, a very important starting material for the manufacture of numerous products.

The steady search for new raw materials and new intermediate products to be utilised in the manufacture of colours has often been crowned with success. We need only to recall the many intermediate products which have been made available for the production of vat dyes and sulphur colours, and which have led to the discovery of new substances with most valuable properties. Very often new lines of research are not always based upon preconceived theoretical ideas, but are opened up by mere accident. A keen power of observation, however, is the most necessary equipment of the chemist who aims at success.

Coal-tar Colours.

In no branch of technical chemistry has such intense work been performed as in that of the coal-tar colour industry. The outsider long ago may have thought that so much had been accomplished in this field that nothing more was left to be done. The countless dyestuffs, giving all the colours of the rainbow, might well have given rise to the belief that there was already a surplus. But here the course of events was just as it generally is in life. With growing possessions, man's needs and demands also multiply. While people were formerly content to produce with coal-tar colours every possible shade in undreamt-of brightness in the simplest way, they gradually began to make more and more exacting demands as regards fastness. Not only had materials to be dyed a pleasing shade, but they also had to be fast to washing and light. Thus new alluring problems were submitted to the colour-chemist, and his indefatigable efforts have already carried him a long way towards the desired end. Strange to say, among the public, you will frequently meet the view that artificial colours do not give fast dyeings. This is a decided error which cannot be too emphatically contradicted. To-day we can produce almost any shade with any desired degree of fastness on any kind of material, whether it be wool, cotton, silk, or paper. If the dyer does not always produce such shades it is the fault of the trade which does not express its demands forcibly enough. Of course, the dyeing with fast colours entails a somewhat greater expense which must naturally be borne by the consumer.

Just at this point, before discussing the progress made in the manufacture of fast colours and in order to prevent misunderstanding, I should like to emphasise the fact that the old colours, though not as fast as those more recently discovered, and though, perhaps, quite fugitive in some respects, still have a right to exist. It would be quite foolish to dye certain kinds of paper intended to be in use for only a very short time with colours absolutely fast to light, or to dye cloth never to be washed with expensive colours fast to washing; or, again, to treat lining, which is but slightly exposed to sunlight, in the same way as materials which must be exceedingly fast to light. Everything according to reason. For many purposes, however, the need for shades fast to light or to both light and washing is so great that it must be given every consideration. How mortifying it must be to notice shortly after you have decorated the walls of your home with most beautiful and expensive materials that the lovely colours daily grow more unsightly, and to see a solitary patch showing up in all its pristine glory amidst a faded background when a picture or other piece of furniture is moved to another place. As it is possible to guard ourselves against such occurrences, we should certainly do so. To-day we are able to produce the most beautifully coloured wall coverings, whether of paper or of woven or printed fabrics, to meet every requirement in regard to fastness. This is proved by the large collection of all kinds of woollen and cotton fabrics (after washing and exposure to light), and especially of wall papers, of carpets, rubber material, and balloon coverings, which the different firms of the German colour and dyeing industry have placed at my disposal for exhibition.

If you now inquire how chemists have been able to make such great progress, my only answer is by logical and untiring efforts along well known ways, undaunted by failures, and by diligently following any track, however, faint, that gave promise of advance.

In every branch of the colour industry these methods have led to faster and even faster dyestuffs, from the multi-coloured benzidine colours, described as fugitive to light and not stable to washing, to the anthraquinone colours and the indigoid vat dyes. In all these classes we have gradually learned to recognise certain regularities and to accomplish certain results by systematically grouping the components and fixing the position of the substituting groups; thus we have succeeded in increasing the fastness to light of the individual chemical according to a preconceived plan.

Indigoid Colours.

The synthetic production of colours allied to indigo was stimulated by the successful synthesis of indigo which almost entirely displaced natural indigo, and called the attention of both chemists and consumer in an increased measure to the advantages of vat-dyeing. The king of dyestuffs, indigo, now finds itself in the company of a whole series of other colours, the brome indigos, the thio indigos, and alizarine indigos, the shades ranging from blue to red, violet, grey, and black. Even the "purple" of the ancients has been reproduced by Paul Friedlaender, who by isolating the dyeing principle found in certain

glands of the purple snail living in the Mediterranean, has demonstrated the fact that this natural colour is identical with a dibrom-indigo which had been long before produced synthetically. These indigoid colours possess the same, if not better, properties than indigo itself.

Alizarine Colours.

The fastness of the alizarine colours, *e.g.*, alizarine red, used for Turkey red, was well known in ancient times. But, whereas formerly only mordant colours were considered to be fast, and consequently only these were looked for in the anthraquinone group, which led to the discovery of alizarine-orange, -brown, -blue, and the alizarine cyanines, Robert E. Schmidt in 1894—1897 succeeded in finding acid-dyeing anthraquinone colours which dye every shade, rivalling the old and well known triphenylmethanes in brightness and simplicity of application, and the alizarine mordant colours in their extraordinary fastness to light. I merely mention alizarine-cyanine-green, alizarine-sky-blue, anthraquinone-blue, alizarine-sapphirole, astrol, -irisol, and -rubinol. Their fastness to light is so excellent that in the famous "Manufacture Nationale du gobelins" in Paris, they have replaced the older dyestuffs for the dyeing of wool used in the manufacture of gobelins. This means a great deal if it be borne in mind that a square metre of these gobelins, for the production of which an operator needs more than a year, costs, on the average, about 6000 francs.

(To be continued).

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, May 1st, 1913.

Sir ARCHIBALD GEIKIE, K.C.B., President, fn the Chair.

PAPERS were read as follows:—

"*The Capacity for Heat of Metals at different Trmperatures.*" By Prof. E. H. GRIFFITHS, F.R.S., and EZER GRIFFITHS, B.Sc.

The thermal capacity, at various temperatures between 0° and 100°, of the following metals has been determined:—Cu, Al, Fe, Zn, Ag, Cd, Sn, and Pb. The work at lower temperatures will be published later.

The heat was supplied electrically, and the conclusions are not dependent upon any assumption concerning the capacity for heat of bodies other than those under consideration.

The temperature range through which the metal was raised was small, about 1·5°, and was measured by differential Pt thermometers. Large masses (1 to 4 kilos.) were employed, and special efforts were made to secure samples of high purity.

The apparatus was constructed with all parts duplicated. The metals examined were suspended by quartz tubes in similar air-tight brass cases, which were placed side by side in a large tank containing rapidly stirred water or oil. The tank was electrically controlled with great constancy at the required temperatures.

One of the metal blocks remained at the tank temperature throughout an experiment; the other, having been previously cooled below the tank temperature, was raised to a somewhat similar temperature above it by a supply of heat electrically developed in the centre of the block, the difference in temperature between the two blocks being determined at regular intervals. Two entirely different methods were employed, and the experimental conditions were varied greatly.

The variation in the thermal capacity can be represented (over the range 0° to 100°) by the following parabolic equations, the difference between the calculated and experimental values in no case exceeding 0·2 per cent. In the large majority of cases the difference is less than 0·1 per cent.

Cu	$s = 0{\cdot}09088$	$(1 + 0{\cdot}0005341t - 0{\cdot}00000048t^2)$,
Al	$s = 0{\cdot}20957$	$(1 + 0{\cdot}0009161t - 0{\cdot}0000017t^2)$,
Fe (ingot)	$s = 0{\cdot}10452$	$(1 + 0{\cdot}001520t - 0{\cdot}0000061t^2)$,
Zn	$s = 0{\cdot}09176$	$(1 + 0{\cdot}0005605t - 0{\cdot}0000178t^2)$,
Ag	$s = 0{\cdot}05560$	$(1 + 0{\cdot}0003396t - 0{\cdot}0000014t^2)$,
Cd	$s = 0{\cdot}05475$	$(1 + 0{\cdot}000520t - 0{\cdot}0000007t^2)$,
Sn	$s = 0{\cdot}05363$	$(1 + 0{\cdot}0006704t - 0{\cdot}0000045t^2)$,
Pb	$s = 0{\cdot}030196$	$(1 + 0{\cdot}000400t - 0{\cdot}0000036t^2)$.

Many forms of equations were tried, but it was found that the experimental results were more closely represented by the parabolic than by any other form.

"*Transition from the Elastic to the Plastic State in Mild Steel.*" By A. ROBERTSON, M.Sc., and G. COOK, M.Sc.

The paper deals with the reduction of stress at the yield point in mild steel. Apparatus for limiting the extension during yield to a value comparable to the elastic extension and for securing axial loading are described. Under these conditions twelve specimens were tested, and a reduction of stress of 24 to 36 per cent observed in eleven, and of 17 per cent in the other one.

Confirmatory evidence of the magnitude of the reduction of stress is adduced from experiments in bending and torsion.

Equations are obtained connecting the stress reduction with the moment and the displacement.

"*Studies of the Processes Operative in Solutions.* XXVIII. *The Influence of Acids on the Rotatory Power of Cane-sugar, of Glucose, and of Fructose.*" By F. P. WORLEY.

Experiments on the hydrolysis of cane-sugar by solutions of benzenesulphonic acid have confirmed the conclusion previously arrived at from those in which sulphuric acid was used, that the ratio of the negative optical rotation at the completion of hydrolysis to the initial positive rotation increases rapidly as the concentration of the acid is increased. The increase is proportional to the concentration of the acid, and in the case of benzenesulphonic acid amounts to about 20 per cent when the concentration is increased from zero to twice normal.

It has been found that the increase is due entirely to the influence of the acid on the rotatory power of the three sugars, cane-sugar and glucose being made somewhat less dextro-rotatory and lævulose considerably more lævo-rotatory by the presence of the acid.

"*Attainment of High Potentials by the Use of Radium.*" By H. G. J. MOSELEY.

A radio-active substance which emits β-radiation should, when insulated, continue to gain a positive charge until a potential of the order of a million volts is reached. Experiments have been made to test this point. A small bulb containing radium emanation was supported by a quartz rod at the centre of a highly exhausted flask. A disk suspended from a quartz spring in the neck of the flask formed a simple attracted disk electrometer. It was found that a bulb of 9 mm. diameter reached a potential of 160,000 volts in the course of a few minutes. A sudden discharge then occurred through the residual gas in the flask. A bulb of 5 cm. diameter charged up much more slowly; no discharge took place, and the final potential 110,000 volts was limited by a leak of electricity along the quartz support.

"*Decrease in Velocity of α Particles in passing through Matter.*" By E. MARSDEN, M.Sc., and T. S. TAYLOR, Ph.D.

The relative velocities of the α-particles of radium C before and after passing through foils of various thicknesses have been investigated by means of the deflection caused by a magnetic field. Tables are given showing the results for gold, copper, aluminium, mica, and air. Down to a velocity of 0·41 of the initial velocity the relation

between velocity V and distance traversed x is shown to be practically $V^2 = k(R-x)$ for air, where k and R are constants. The relation alters with increasing atomic weight of the absorber until it approximates more nearly to $V^2 = k(R-x)$ for gold. However, with none of the absorbing substances was it possible to obtain a beam of α-particles of velocity less than 0·415 of the initial velocity, this value being reached in each case for an absorption foil of 6·5 cm. air equivalent. With further thickness of absorber the velocity apparently remains constant although the number of a-particles in the beam diminishes rapidly with increasing thickness up to 6·94 cm. air equivalent.

CHEMICAL SOCIETY.

Ordinary Meeting, April 17th, 1913.

Prof. W. H. PERKIN, LL.D., F.R.S., President, in the Chair.

(Concluded from p. 228).

107. "*A New Variety of Manna and a Note on the Melting-point of Dulcitol.*" By JOHN RALPH FURLONG and LAWRENCE EVERSLEY CAMPBELL.

A specimen of leaves and twigs partly covered with a white incrustation ("manna") was received recently at the Imperial Institute from Mr. C. N. B. Venables, North Western Rhodesia. The plant was identified at the Royal Botanic Gardens, Kew, as a *Gymnosporia*, sp., probably *G. deflexa*, Sprague.

The incrustation had a slightly sweet taste, and was for the most part evenly deposited. It could be easily separated from the leaves and twigs, and contained 4·9 per cent of moisture. On dissolving the manna in a small quantity of hot water and adding alcohol to the filtered solution, a crystalline substance separated in highly lustrous prisms melting at 183° (uncorr.) and 188° (corr.). This substance was optically inactive, even in the presence of borax, and did not reduce Fehling's solution either before or after heating with dilute acid. On oxidation with nitric acid it yielded mucic acid, and on acetylation gave a hexa-acetyl derivative melting at 171° (corr.). These results prove that the crystalline substance is dulcitol; it was isolated to the extent of 54 per cent of the weight of manna used.

The residue of the manna after the removal of the dulcitol was a pale brown, sweet, gummy material, which reduced Fehling's solution, and gave indications of the presence of a furfuraldehyde-yielding complex. It contained 6·4 per cent of reducing sugar, calculated as dextrose, and after heating with dilute acids yielded reducing sugar equivalent to 6·6 per cent of sucrose, these two figures being expressed on the original manna. The residue could not be further examined owing the small quantity available.

Some confusion appears to exist in the literature as to the melting-point of dulcitol; for example, Beilstein, Abderhalden, Richter, and Watts in their handbooks give 118—189°, without stating that this is a corrected figure. Lippmann (*Ber.*, 1892, xxv., 3217) identified as dulcitol a substance which melted at 188° (uncorr.).

A sample of dulcitol (Kahlbaum) after repeated recrystallisation from alcohol, melted at 183° (uncorr.) and 188° (corr.).

108. "*Blue Adsorption Compounds of Iodine.* Part II. *The Influence of Constitution on the Adsorption by 2- and 4-Pyrone Derivatives.*" By GEORGE BARGER and WALTER WILLIAM STARLING.

In a previous paper (Barger and Field, *Trans.*, 1912, ci., 1394), the colloidal properties of the blue substances were described which are formed by iodine with starch, cholalic acid, and saponarin. The phenomenon has since been found to be quite general, and occurs with some fifty of the substances which the authors have so far examined. In one case, that of napthaflavone, the reaction is even more delicate than with starch, and a blue coloration is produced in solutions containing 1 part of iodine in 800,000 parts of water.

The power of adsorbing iodine seems to depend on the presence of a crossed conjugated linking, and on the residual affinity of oxygen (or sulphur). It is by no means confined to pyrone derivatives. It is greatly increased by benzene nuclei, as in the coumarins, chromones, xanthones, and flavones; alkyl- and hydroxy-groups diminish it. Thus coumarin adsorbs slightly, hydrocoumarin and hydroxycoumarins not at all; naphthacoumarin, phenylcoumarins, and benzoyloxycoumarins are coloured blue by very dilute iodine solutions.

The authors have thus, for the first time, been able to examine the effect of the chemical constitution of the adsorbent, and their results agree closely with those already obtained by Freundlich and others in the study of the converse phenomenon, that is, the capacity of various organic substances of being adsorbed by the same adsorbent (charcoal).

The general conclusions of the first paper have been confirmed and extended. In no single case is the iodine taken up in stoichiometrical proportions, although many of the blue substances can be obtained crystalline.

109. "*Reactions of Halogen-substituted Acids.* Part I. *The Action of Sodium Hydroxide and Methoxide in Methyl-alcoholic Solution on Bromoacetic, α-Bromopropionic, and Monobromosuccinic Acids.*" By ERIC HOST MADSEN.

The effect of methyl-alcoholic solutions of sodium hydroxide and sodium methoxide on various bromine-substituted acids has been examined. Both reagents give rise to the methoxy-derivative in the case of bromoacetic and α-bromopropionic acid, whereas monobromosuccinic acid gives the corresponding methoxy-acid with sodium methoxide, but malic acid with sodium hydroxide, both reactions being accompanied by the formation of some fumaric acid.

In the case of the two first acids the velocity of reaction is the same for both sodium hydroxide and methoxide, but with bromosuccinic acid sodium hydroxide reacts with the greater velocity. The order of reaction is different with the three acids; α-bromopropionic acid gives a reaction of the first order, bromoacetic acid one of the second order, and bromosuccinic acid one of a higher order, which was not determined.

110. "*The Preparation and Analysis of Methane.*" By COLIN CAMPBELL and ALBERT PARKER.

Methane was prepared by the action of hot water on pure aluminium carbide. Acetylene was removed by means of an ammoniacal solution of cuprous chloride. The gas was freed from hydrogen by first adding a slight excess of oxygen, and then passing the mixture over palladium black at 90° to 100°. Analysis showed the methane to be practically pure. A method of analysis was devised, by which 0·05 per cent of hydrogen could be estimated.

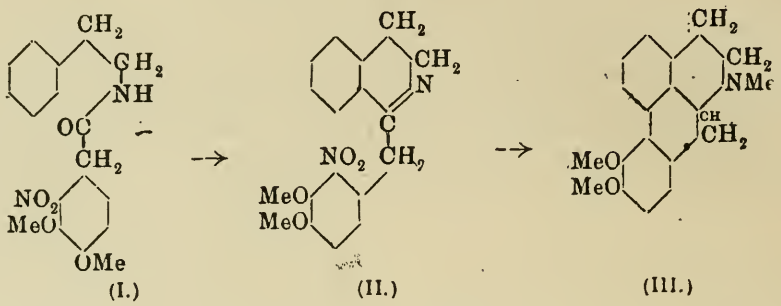
111. "*Influence of Increase of Initial Temperature on the Explosiveness of Gaseous Mixtures.*" By ALBERT PARKER.

Mixtures of methane, carbon monoxide, hydrogen, and coal-gas were made with oxygen and with air, and sparked in a eudiometer tube at the ordinary temperature and at 100° under various pressures. It was found that increase of initial temperature decreased the values of the lower limits of explosibility of the above gases. It was also found that the values of the lower limits of explosibility of methane, carbon monoxide, and coal-gas were higher for mixtures with oxygen than for mixtures with air.

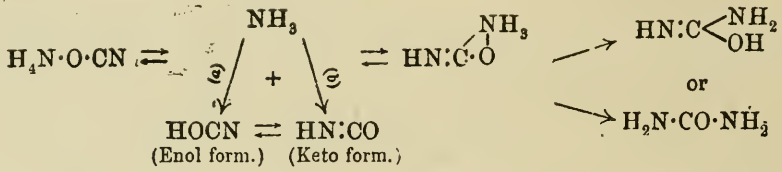
112. "*Keto-enolic Tautomerism and the Absorption Spectra of the Aliphatic Ketones.*" By HARRY MEDFORTH DAWSON.

From an examination of the data expressing the rate at which the aliphatic ketones react with sodium hydrogen sulphite and hydroxylamine, it was shown that these

A.



B.



reactions have no connection with the intramolecular change of linking associated with the keto enolic transformation. These data cannot therefore be cited in support of the view that selective absorption in the ultra-violet is connected with the intramolecular change of linking involved in the transfer of a labile hydrogen atom (compare Baly and Desch, *Trans.*, 1904, lxxxv., 1029; 1905, lxxxvii., 766; Stewart and Baly, *Trans.*, 1906, lxxxix., 489).

The interpretation of absorption spectra and of extinction curves was discussed, and it was shown that the so-called persistence of a selective absorption band is of no particular value. In order to obtain comparative numbers representing the selective absorption capacities of the individual members of a group of similar substances, measurements are required which will afford a means of ascertaining the relative thicknesses of layers of equimolar solutions which give rise to the same amount of selective absorption.

The absorption coefficients of the aliphatic ketones for light of the frequency supposed to be characteristic of the $\cdot CH_2 \cdot CO \cdot$ group were shown to have no connection with the corresponding rates of isomeric change. Furthermore, in the case of acetone it is found that when the rate of isomeric change is increased to something of the order of 100,000 times, there is practically no alteration in the absorption of the characteristic ultra-violet radiation. These facts indicate that the behaviour of the simplest keto-enolic tautomerides is absolutely incompatible with the Baly-Desch theory.

113. "*Experiments on the Synthesis of* Apomorphine." By FRANCIS WILLIAM KAY and AMÉ PICTET.

With the object of synthesising *apo*morphine, the authors have attempted the preparation of 2-nitroveratryldihydro-*iso*quinoline (II.), by means of reactions already described by them (*Ber.*, 1909, xlii., 1973). On submitting such a derivative of *iso*quinoline to a treatment similar to that described by Pschorr (*Ber.*, 1904, xlii., 1926), and by Gadamer (*Arch. Pharm.*, 1911, 680, p. 249), for the conversion of nitropapaverine into *dl*-glaucine, it would be expected to yield the dimethyl ether of *apo*morphine (III.). (See A, above).

Although 2-*nitrohomoveratroyl*-3-*phenylethylamine* (I.) does actually lose water when heated with phosphoric oxide in solution in boiling toluene, yet it fails to yield a derivative of *iso*quinoline by ring-formation as would be expected, a yellow indifferent substance, m. p. 129°, being obtained instead. This dehydro-product is still a derivative of phenylethylamine, for when reduced with tin and hydrochloric acid it yields that base.

o-*Nitrophenylacetyl*-β-*phenylethylamine*, colourless crystals, m. p. 97—99°, fails to lose water when submitted to the action of phosphoric oxide in boiling xylene.

114. "*The Absorption Spectra of various Derivatives of Benzene.*" By JOHN EDWARD PURVIS and NIAL PATRICK MCCLELAND.

The absorption spectra of the vapours, solutions, and thin films of some of the simpler benzene derivatives have been compared, and particularly various nitro-compounds. The results were discussed from a consideration of the oscillations of different electronic centres.

115. "*Notes on the Determination of the Electrical Conductivity of Solutions.*" By HAROLD HARTLEY and WILLIAM HENRY BARRETT.

The electrical resistance of aqueous solutions of potassium chloride has been measured by a telephone and induction coil, and also by the rotating commutator and galvanometer, and it has been found that the two methods yield different values for the resistance. The values found by the telephone are about half a per cent lower than those found by the second method. A new form of conductivity cell has been devised for use with dilute solutions of aqueous and non-aqueous solutions in which the solvent is protected from contact with atmospheric impurities.

116. "*Mechanism of the Transformation of Ammonium Cyanate into Carbamide, and of the Decomposition of Carbamide by Heat. The Polymerisation of Cyanic Acid.*" By EMIL ALPHONSE WERNER.

It was pointed out that the theory recently put forward by Chattaway (*Trans.*, 1912, ci., 170) to explain the transformation of ammonium cyanate into carbamide, and the formation of biuret and cyanuric acid from the latter is open to serious objection, since it fails to account for several of the phenomena connected with the changes, and is not in agreement with others. The reversible reactions given by Chattaway, namely,—

$$H_4N \cdot NCO \rightleftarrows H \cdot N{:}C{:}O + NH_3 \rightleftarrows HN{:}C{<}^{OH}_{NH_2},$$

is difficult to conceive, cyanic acid being supposed to have the fixed constitution $H \cdot N{:}C{:}O \cdot$.

The whole series of changes, it was shown, can be easily explained and understood by taking into consideration the

two fundamental causes, namely, dissociation and the reversible change,—

$$HO{\cdot}CN \rightleftharpoons HN{:}CO,$$

and no hypothetical intermediate compounds are required to help the explanation. Thus, the accompanying scheme explains the formation of carbamide. (See B, p. 136).

The lower temperature being favourable to reaction (*a*), the higher to reaction (*b*), whilst biuret results from the interaction of carbamide and cyanic acid, as has been proved by direct experiment. A theoretical explanation of the formation of cyanuric acid and cyamelide respectively from cyanic acid was given, based on the existence in equilibrium of the two forms of the acid. The sublimates formed when carbamide and biuret are decomposed by heat were shown to consist of ammonium cyanate and carbamide in variable proportions according to the experimental conditions, and the general impression that carbon dioxide is a product of the decomposition of carbamide by heat was shown to be unfounded; the vapours evolved consist solely of ammonia and cyanic acid.

117. "*Non-aromatic Diazonium Salts.* Part I. *Antipyrinediazonium Salts and their Azo-derivatives.*" By Gilbert T. Morgan and Joseph Reilly.

1-Phenyl 2 : 3-dimethylpyrazolone-4-diazonium chloride and the other diazonium salts previously described (*Proc.*, 1912, xxviii., 334) coupled readily with aromatic amines and the aliphatic β-diketo-compounds.

1-Phenyl 2 : 3-dimethylpyrazolone-4-azo-β-naphthylamine (m. p. 234—235°), unlike the purely aromatic azo-β-naphthylamines, yielded intensely dark purple salts, stable in aqueous solution.

1-Phenyl-2 : 3-dimethylpyrazolone-4-azoacetylacetone (m. p. 181—182°) gave rise to an orange sparingly soluble sodium derivative, developing the enolic red coloration with ferric chloride, and yielding an olive-green copper derivative.

Ethyl 1-phenyl-2 : 3-dimethylpyrazolone-4-azoacetoacetate (m. p. 174—175°) resembled the foregoing compound.

The coupling of antipyrinediazonium salts and methyl acetylethyl ketone (acetylmethylacetone) was accompanied by the elimination of an acetyl group, so that the resulting condensation product, m. p. 199—200°, is derived from methyl ethyl ketone or dimethyl diketone (diacetyl), according as to whether it is to be regarded as an azo-derivative or a hydrazone.

118. "*The Fractionation of Alloys and Minerals in the Electric Micro-furnace.*" By Arnold Lockhart Fletcher.

An instrument—the micro-furnace—was described for a rapid qualitative and quantitative analysis of small quantities of alloys, The method described amplifies the classification of the more refractory alloys (Turner, *Trans.*, 1912, ci., 585).

PHYSICAL SOCIETY.

Ordinary Meeting, April 25th, 1913.

Prof. C. H. Lees, F.R.S., Vice-President, in the Chair.

A paper on "*A Graphical Method of Optical Imagery*" was read by Mr. W. R. Bower.

The paper contains a development of optical imagery based on elementary geometry, including limiting positions, but excluding cross-ratios, centres of perspective, &c. The method adopted is useful for teaching the properties of optical systems to those who are not essentially students of pure mathematics, and can be very satisfactorily used by those capable of draughtsmanship with mathematical instruments.

The principle of the method is as follows:—The vertex (object) of a small incident pencil of rays is considered to move along a line parallel to the principal axis of the optical system. This line is also regarded as the incident portion of a fixed ray. Then the directions of the ray after reflection or refraction at the several surfaces do not alter as the position of the object changes. They are therefore the fixed loci of the images or vertices of the reflected and refracted pencils. Then the successive positions of the image resulting from a progressive movement of the object are obtained. Also the constructions are such that in the case of a thick lens the importance of the cardinal points and planes is demonstrated.

First, considering refraction at a spherical surface and assuming that μ is the relative velocity of light in the two media, a construction for the refracted portion of any incident ray is obtained from the wave principle; then the sine law of refraction and the position of the aplanatic pair of points are deduced.

When the incidence is normal it is convenient in drawing to increase largely the scale of length perpendicular to the principal axis in comparison with that along the principal axis. A distorted figure is obtained, but the relative lengths of lines perpendicular to the axis or of lines parallel to the axis will be maintained.

The principal foci for normal incidence on a single spherical refracting surface are obtained, and then the usual algebraical expressions are deduced from the figure. A convenient construction for finding the principal foci and aplanatic pair of points when μ and r are given is then shown.

For a thick lens it is most convenient to assume that the two surfaces separate three different media. After obtaining the refracted portions of a ray—called the second fixed ray—incident parallel to the principal axis of the system, the positions of the cardinal and nodal points and planes are indicated and their more important properties deduced. A convenient construction is shown for finding the cardinal and nodal points, when r_1, r_2, μ, μ' are given. At the same time the course of the first fixed ray is determined. The first fixed ray is defined as the ray which emerges from the system in the same line as the incident portion of the second fixed ray obtained above. There is also a visualisation of the Gauss and Abbe definitions of focal length. The usual algebraic relations are deduced. After a discussion of magnification—lateral, axial, and angular—it is shown that when the six cardinal points of one optical system are combined with those of another a resulting set of six cardinal points is obtained, and thus a composition of the cardinal points of various optical systems may be effected.

Returning to refraction at a single spherical surface the cases of meridian and sagittal rays are separately considered. For the former the position of Cornu's junction point is obtained in a simple manner. Finally, the usual algebraic relationships are deduced, and a graphic construction for points on a caustic is given.

The Chairman stated that he understood the present paper to be a systematic carrying out of the method explained at the commencement of the paper. He would like to know what the author's experience in teaching the method had been.

Dr. W. H. Eccles remarked that the paper was essentially an educational one. It led to no new or novel results, but it did, so to speak, drive a lane through the subject and give new points of view. He did not think the method would be very successful in teaching beginners unless as a laboratory method. He regarded it more as a paper for teachers than for students.

The Author, in reply, stated that the object of the paper was to give a way through the subject. He found that students who worked through graphical methods did get an understanding of the subject that those who glibly worked with equations failed to get. In optics he considered there was a need for methods which visualised things more definitely.

Mr. T. Smith has communicated some remarks on the above paper. These will appear in due course in the *Proceedings*.

A paper on "*The Spectroscopic Resolution of an Arbitrary Function*" was read by Dr. C. V. BURTON.

An ordinary grating has periodic rulings, and a spectrum obtained by means of it is characteristic of the radiation entering the spectroscope-slit. But if the radiation is homogeneous, while the distribution of the rulings is arbitrary, we obtain a spectrum characteristic of the grating. It is thus found to be theoretically possible to resolve spectroscopically a given arbitrary function $\phi(x)$ into its harmonic constituents. The "permeability" of a photographic negative at any point being defined as the square root of the reciprocal of the "density," the first step is to make an "equivalent grating." This is a plate whose permeability (variable in one dimension only) has at any point x the value $A+B\phi(x)$, where A and B are constants. When this (transmission) grating takes its place in a spectroscope whose slit is fed with homogeneous light, the spectrum of the function $\phi(x)$ can be seen or photographed. Suitably interpreted, it gives us the periodogram of $\phi(x)$. A device is described which it is hoped may prove useful for determining the phases of the various harmonic constituents.

The theory of the proposed method of resolving functions is discussed, and is as complete as that of ordinary spectroscopy, while in one respect it is more simple; for, since the light entering the spectroscope-slit is entirely of one wave length, the comparison of intensities of spectral lines (whether visually or photographically) is facilitated.

Some preliminary practical tests are now being made.

Lord RAYLEIGH communicated the following remarks:—In connection with Dr. Burton's interesting paper I should like to draw attention to somewhat similar suggestions that I made in 1903 (*Phil. Mag.*, v., 238). It is to be wished that one or other of these optical methods should be applied to some practical problem of the analysis of an irregular curve.

The CHAIRMAN remarked that those who had gone through the labour of getting out a periodogram would appreciate any mechanical means of doing this. He understood that Dr. Burton considered Lord Rayleigh's method was better than his own.

The AUTHOR stated that he thought that Rayleigh's method had great advantages. In reply to Dr. A. Russell, he also stated that the phase of the harmonic components could be determined, but with an ambiguity of half a period. This ambiguity could be removed by a rough integration over a portion of the curve.

Mr. J. E. SEARS asked if all the periods given by this method of analysis were multiples of a fundamental as in the cases of the ordinary Fourier's analysis.

The AUTHOR stated that the present method gave the periodogram of a function as it was given by Fourier's double integral theorem. In reply to a further question from the same speaker, he stated that, in analysing a column of numerical values, the method would give all the detail that was actually involved in the figures themselves.

Mr. A. EAGLE (communicated remarks) thought it ought to be clearly pointed out that if it was desired to analyse a function extending over a limited range into the ordinary Fourier's series, it would be necessary to repeat this function end to end a very large number of times in the grating. If it was only inserted once in the grating we should get the Fourier integral analysis of a function, equal to the given function within the given limits, but zero everywhere outside these limits, which was quite a different thing. For any periodic function stretching from $-\infty$ to $+\infty$, it was easily seen that Fourier's integral broke down into a Fourier's series. Obviously, in this case, the periodogram must vanish for all wave-lengths that are not aliquot parts of the wave-length of the function analysed.

The AUTHOR entirely agrees with Mr. Eagle's remarks. So far he has not contemplated the application of his method to strictly periodic functions, because the coefficients of their various harmonic constituents can be so readily obtained by mechanical integration or otherwise.

SOCIETY OF CHEMICAL INDUSTRY.

(LONDON SECTION).

Ordinary Meeting, May 5th, 1913.

Prof. W. R. HODGKINSON in the Chair.

THE following papers were read and discussed:—

"*The Methods and Apparatus used in Petroleum Testing.* II. *Viscometry.*" By W. F. HIGGINS.

This paper forms part of a research on the methods and apparatus used in petroleum testing, now being carried out at the National Physical Laboratory in connection with the work of the International Commission for the Unification of Tests on Petroleum Products.

The instruments dealt with were the Engler and Redwood viscometers. In these instruments a measure of the viscosity of a liquid is obtained by noting the time of outflow of a definite quantity of the liquid, from a vessel of known dimensions, through a jet of specified size. The results obtained are necessarily only of comparative value since the time of flow is a function of the dimensions as well as of the viscosity. Accordingly, the usual procedure is to compare the time of outflow of the liquid under test with that of a standard substance. In the Engler apparatus the liquid chosen is water, while for the Redwood apparatus the results are referred to refined rape oil.

The object of the present work was to find a relation between the readings of the instruments and the absolute viscosity of the liquid under test. An accurate knowledge of the temperature is of unusually great importance in the viscosity determination of an oil. The temperature variation of viscosity (large with nearly all liquids) amounts with some oils to as much as 8 per cent per 1° C., so that very careful temperature adjustment is of the utmost importance in experimental work.

The absolute viscosities were determined by a capillary tube method. The apparatus employed consisted essentially of two vertical tubes joined at the lower ends by a capillary tube of suitable dimensions. Arrangements were made so that the upper end of either of the vertical tubes could be connected to a reservoir of air under known pressure or to the atmosphere as desired. The liquid contained in the tubes could thus be forced through the capillary in either direction. The time taken for a definite quantity of the liquid to flow through the capillary tube was determined from observations of the transits of the meniscus across two marks on either of the vertical tubes. The corresponding volumes were measured in a separate experiment. The vertical tubes with the capillary joining them were completely immersed in a well-stirred water-bath provided with electric heating coils, which enabled the temperature to be maintained at any desired value.

The oils employed had viscosities ranging from 0·02 to 9 cc. units, the corresponding times of outflow using the Redwood viscometer being from 30 to 4000 seconds approximately. Curves and tables have been constructed correlating these values, and it is found that the absolute viscosity may be deduced from the time of flow on the Redwood instrument by the use of a formula of the type—

$$\eta = \left(A t - \frac{B}{t}\right)\delta,$$

where A and B are constants depending upon the dimensions of the apparatus, t is the time of outflow (in seconds), δ is the density of the liquid (grms. per cc.), and η is its viscosity (cc. units). The values of A and B for an instrument of normal dimensions are—

$$A = 0{\cdot}00260 \qquad B = 1{\cdot}715.$$

Experiments were also carried out on the Engler apparatus, and a table has been drawn up showing the relation between the results obtained with this instrument and with the Redwood viscometer.

"*Ore Deposits of Hu-Nan and Hu-Peh.*" By W. R. SCHOELLER.

The following deposits are described:—

1. *Stibnite Deposits of Central Hu-nan.*—The district situated between the Siang and Yuen Rivers produces ore averaging 58 per cent Sb. There are no mines in the European sense of the term. Crude antimony is obtained at Chang-sha and Yi-yang.

2. *Lead-zinc Ores of Southern Hu-nan, South of Heng-chow.*—The most important mine in the district is the Sui ku-shan mine, owned by the Hu-nan Board of Mines. The ores are argentiferous galena, blende, and mixed sulphides. The best lead ore assays 30—40 ozs. of silver, 72 per cent lead, and 3 per cent zinc. The natives extract silver from galena, and work zinc blende for spelter.

3. *Realgar Deposits near Li, North Hu-nan.*—These deposits of considerable magnitude average 95 per cent As_2S_2.

4. *Copper Ores in Hu peh.*—A rich copper district is situated near Ching-kno, East Hu-peh. The outcrop show enriched sulphides; silver is always present, while gold is frequent.

"*Experiments on the Hydrometallurgical Treatment of Copper Slimes.*" By W. R. Schoeller.

Experiments on the recovery of copper of slimes were undertaken with a view to dealing with the slimes at the same rate as they were produced at the dressing-plant.

The material experimented upon was obtained from a large smelter in the United States, and contained 2·85 per cent copper.

Electrometallurgical tests proved a failure, the rate of extraction being below 0·1 per cent per twelve hours. Ferric sulphate and cupric chloride did not extract well.

After a light calcination, cold dilute sulphuric acid and sulphurous acid dissolved 90 per cent of the copper.

The recovery of copper by means of a sulphatising roast and leaching appears to be the best process if it can be done at a profit.

The process is briefly described, and the cost of the various operations discussed.

"*Hydrazine Nitrate.*" By W. R. Hodgkinson.

In connection with experiments on the removal of metallic fouling from guns, a comparison was made of the properties of ammonium and hydrazine nitrates.

Hydrazine nitrate is a little less deliquescent than the ammonium salt, and although more soluble in cold water it is insoluble in alcohol. The dry salt melts at 70°, and may be kept at 100° for long periods without serious decomposition. At about 150° it inflames, and burns quietly. It explodes with considerable violence when heated in a closed vessel. In a vacuum it is decomposed by heat into water, nitric oxide, and nitrogen.

Contact with peroxides or permanganates inflames the dry salt.

Most metals have but little action on a strong solution, and when the salt is fused in contact with them it inflames more quickly than when alone, the metal suffering some oxidation. A notable exception was found with nickel and cobalt. A very violent explosion occurs as soon as pieces of these metals ("cubes") come in contact with the fused salt, although the addition of these metals as sheet or wire caused no explosion.

The cause of the action with nickel and cobalt has not yet been explained.

Determination of Nitrites in Potable Waters.—Maurice Lombard.—One grm. of sulphanilic acid is dissolved in 100 cc. of a saturated solution of pure ammonium chloride, and 1·5 grm. of phenol and 100 cc. of 2·N HCl are added. Then 1 cc. of the nitrite solution is added to 50 cc. of this reagent, it is allowed to stand f r a quarter of an hour, excess of ammonia is added, and the coloration is compared with that of potassium bichromate solutions, which are prepared for the purpose and standardised with known nitrite solutions.—*Bull. Soc. Chim. de France*, xiii.-xiv., No. 6.

NOTICES OF BOOKS.

A Foundation Course in Chemistry for Students of Agriculture and Technology. By J. W. Dodgson, B.Sc. (Lond.), and J. Alan Murray, B.Sc.(Edin.). London, New York, Bombay, and Calcutta: Longmans, Green, and Co. 1913.

Students who are attending short courses in agriculture, horticulture, dairy work, domestic economy, &c., will find that this book contains a satisfactory account of the fundamental principles of chemistry, written from the point of view of their special requirements. The chemistry of the air, water, limestone, common salt, &c., are discussed in the early chapters, and the general principles of the science are adequately explained. Later chapters deal with organic matter, the paraffins, coal-tar, &c., and it seems not improbable that in some respects they would be a good deal above the heads of those who had acquired all their knowledge of chemistry from the book. However, the number of technical students who have left school without learning any chemistry whatever is rapidly diminishing, and those who had worked through even a very elementary course would find this book a useful introduction to their technical work. It contains a number of questions, some of which are fairly difficult, and problems for numerical calculations, with answers to the latter.

Exercises in Gas Analysis. By Dr. Hartwig Franzen. Translated by Thomas Callan, M.Sc. (Manc.), Ph.D. (Heidelberg), F.C.S. London, Glasgow, and Bombay: Blackie and Son, Ltd. 1913.

This little book is intended to serve as an introduction to the larger and more complete works on the subject by Hempel and Winkler, which are hardly suitable for the use of beginners who have had no previous experience of gas analysis. It contains a series of carefully graduated exercises, in the course of which the student would learn the use of all the commoner forms of apparatus for gas analysis, such as the Hempel and Bunte burettes, the Orsat apparatus, &c. The experimental directions are clear and detailed, and sources of error and probable pitfalls are frequently pointed out. Towards the end of the book the treatment of fairly complex mixtures of gases is discussed, and brief explanations of the theoretical questions involved are added. For the purposes of the English translation Prof. Franzen has thoroughly revised the text, and has also made a few alterations in the exercises.

Studies in Soil Catalysis. By M. X. Sullivan and F. R. Reid. Washington: Government Printing Office. 1912.

This Bulletin contains a highly important paper upon the subject of soil fertility, and further accounts of the authors' researches will be awaited with interest. By a series of ingenious and well-planned experiments it has been proved that soils possess in a varying degree the power of decomposing hydrogen peroxide, and that although fertility is not dependent upon the catalytic power, the presence of strong catalytic power may be regarded as evidence that the soil would be highly productive. This catalytic power is checked by certain substances; for example, hydrocyanic acid practically destroys it. The evidence so far accumulated seems to show that the catalytic power is not due to enzymes but to organic or inorganic matter, working either separately or conjointly.

Ausführung Qualitativer Analysen. ("Methods of Qualitative Analysis"). By Wilhelm Biltz. Leipzig: Akademische Verlagsgesellschaft. 1913.

The author of this book has a firm belief in the great value of the study of qualitative analysis, both for its own sake and for the training it gives in accurate habits of thought, in careful manipulation, and in the use of the

reasoning powers. The course which is described in this book should develop the student's initiative and give him a sound knowledge of analytical work. Great stress is laid upon the importance of analysis in the wet way; blowpipe work is given its proper place, and it is impressed upon the student that he must not regard it as a comparatively unimportant and, in fact, almost superfluous introduction to analysis proper. In the courses on analysis in the wet way and on testing for acids there are no very striking novelties of treatment, the usual methods being followed. The author is always careful to choose for description those processes which are at once the most accurate, most rapid, and simplest, and the tendency which he displays towards didacticism is probably no serious drawback to a book intended for the use of elementary students.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Bulletin de la Société Chimique de France.
Vol. xiii.-xiv., No. 4, 1913.

Synthesis of Monosubstituted Paraconic Acids.—Ph. Barbier and R. Locquin.—The condensation of aldehydes with ethyl bromosuccinate is effected rapidly by the use of the alloy of zinc and magnesium, though this method of preparing monosubstituted paraconic acids is not practically advantageous. The yields are better than when Fittig's method is used, but are not good. They appear to improve as the molecular weight of the aldehyde employed increases.

Preparation of Terpenylic and Terebic Acids.—R. Locquin.—Terebic acid can be prepared by the oxidation of methoethylpeptanonolide by means of nitric acid, but at the same time a very large quantity of terpenylic acid is formed. As a matter of fact this method is the best for preparing the latter acid, for the yield obtained is decidedly greater than that given by the action of potassium permanganate or chromic acid on the same olide.

Presence of Stachyose in Seeds of Leguminosæ.—Georges Tanret.—Stachyose is a tetrasaccharide, $C_{24}H_{42}O_{21}$—the first sugar containing C_{24} known—which gives a compound with $Sr(OH)_2$, by means of which it can be isolated. The author has employed this reaction to detect its presence in various seeds, and has found it in all the seeds of the *Leguminosæ* investigated. Stachyose is an alimentary sugar, which is entirely consumed in the organism.

No. 5, 1913.

Absorption Spectra of Fluoresceïn, Eosine, Erythrosin, and Bengal Rose.—MM. Massol and Faucon.—Each of these four substances shows a large absorption band in the green or blue. With fluoresceïn the ultraviolet spectrum shows three absorption bands, eosin gives one band and erythrosin and Bengal rose show progressive absorption without bands. Halogen substitutions modify both the visible and invisible spectra. All the substances can be identified in very small quantities by determining the size of the absorption bands when the thicknesses vary, and by plotting their positions with reference to the green thallium and blue strontium rays.

Action of Thionyl Chloride on 1.4-Lactones.—Ph. Barbier and R. Locquin.—Thionyl chloride reacts with simple 1.4 lactones, such as methyl.4-butyrolactone, to give the chloride of the acid alcohol, the lactonic chain being opened. Unlike the lactones of the fatty series, however, cumarin does not react with thionyl chloride, probably owing to the special constitution of this unsaturated lactone.

Uranium Formate.—Oechsner de Coninck and A. Raynaud.—Uranium formate is a light yellow, deliquescent, soluble salt. When it is subjected to desiccation it gives up formic acid. On boiling with distilled water it gives a yellow precipitate of uranic dihydrate:—

$$\left.\begin{matrix}CHO.O\\CHO.O\end{matrix}\right\} UO_2 + 3H_2O = 2(CHO.OH) + UO_3.2H_2O.$$

Uranium formate is easily decomposed by warm water. With methyl alcohol in diffused light after three months it gives a deposit of uranous oxide, formic acid being liberated. With ethyl alcohol the action is only very slight, and the residue contains a small amount of uranic monohydrate, $UO_3.H_2O$.

Action of Thionyl Chloride on Lactonic Acids.—Ph. Barbier and R. Locquin.—Thionyl chloride in boiling benzene readily opens the lactonic chain of simple butyrolactones (except cumarin). It has no effect upon the lactonic chain of butyrolactones with acid functions. In the case of all the lactonic acids investigated, whatever the quantity of $SOCl_2$ employed, the only action is the formation of the corresponding acid chloride.

Derivatives of Methoxyphenylisoxazolones.—A. Wahl and C. Silberzweig.—The cyclic aldehydes combine readily with the isoxazolones of methoxybenzoylacetic ethers, giving stable crystalline compounds. The phenolic derivatives are soluble in alkalis with colorations ranging from yellow to reddish violet, according to the position of the auxochromes. In presence of an excess of caustic alkali the colour rapidly disappears even in the cold, probably owing to the hydrolysis of the lactonic chain. The authors have also prepared indigoid derivatives of the phenylisoxazolones by the action of the chloride of 5-bromo-isatin. These compounds dissolve in organic solvents giving a red-violet coloration.

MISCELLANEOUS.

Royal Institution.—On Tuesday next, May 20, at 3 o'clock, Prof. T. B. Wood will deliver the first of a course of three lectures at the Royal Institution on "Recent Advances in the Production and Utilisation of Wheat in England"; on Thursday, May 22, Prof. W. J. Pope begins a course of three lectures on "Recent Chemical Advances—(1) Molecular Architecture, (2) Chemistry in Space, (3) The Structure of Crystals"; and on Saturday, May 24, Prof. Rutherford commences a course of three lectures on "Radio-activity—(1) The Alpha Rays, (2) The Origin of the Beta and Gamma Rays, (3) The Radio-active State of the Earth and Atmosphere." The Friday Evening Discourse on May 23 will be delivered by Prof. S. P. Thompson, on "The Secret of the Permanent Magnet"; on May 30 by Dr. Owen Seaman, on "Parody"; and on June 6 by Dr. Francis Ward, on "Reflection and Refraction of Light as Concealing and Revealing Factors in Sub-aquatic Life."

MEETINGS FOR THE WEEK.

TUESDAY, 20th.—Royal Institution, 3. "Recent Advances in the Production and Utilisation of Wheat in England," by Prof. T. B. Wood, M.A.
WEDNESDAY, 21st.—Microscopical, 8. Exhibition of Aquatic Life.
THURSDAY, 22nd.—Royal Institution, 3. "Recent Chemical Advances—Molecular Architecture," by Prof. W. J. Pope. F.R.S., &c.
—— Royal Society, 4.30. (The Bakerian Lecture), "Rays of Positive Electricity," by Prof. Sir J. J. Thomson, O.M., F.R.S.
FRIDAY, 23rd.—Royal Institution, 9. "The Secret of the Permanent Magnet," by Prof. S. P. Thompson, F.R.S.
SATURDAY, 24th.—Royal Institution, 3. "Radio-activity—The α-Rays and their connection with the Transformations," by Prof. E. Rutherford, F.R.S.

THE CHEMICAL NEWS.

Vol. CVII., No. 2791.

THE TEMPERATURE OF SUBLIMATION.

By Prof. JOLY, F.R.S.

In a recent number of the *Philosophical Magazine* (Feb., 1913) I described a simple apparatus (which I have called the Apophorometer), by means of which the chemical analysis of many volatile bodies may be effected by so regulating the temperature of the finely powdered substance as to volatilise one by one its several constituents in the order of their volatility. The successive sublimates are removed in watch-glasses and weighed; the residues also being weighed when desired. I cited several examples of more or less complex mineral bodies quantitatively analysed by fractional sublimation.

I was at the time rather surprised at the apparent sameness of temperature at which certain very different mineral species decomposed, but contented myself by pointing out the probable importance of temperature measurements, and by indicating a method of effecting such measurements. This method—that of determining the temperature in terms of the current which heats the hob upon which the substance reposes—has proved very satisfactory; the current and temperature maintaining a rectilinear relation to at least 1200° C.

Since the writing of my first paper I have been able to observe the temperatures of sublimation of a certain number of typical minerals, and, although more observations are desirable, the approximate agreement among the results obtained, as well as the delay which must attend the acquisition of further material, induce me to give a brief account of what I have observed. I shall refer to three volatile constituents only in this present note: antimony, arsenic, and tellurium. It will be understood that the temperatures given below are approximate only, their value chiefly residing in their comparability. Every precaution was taken to ensure this by making the conditions alike in every case, and allowing a fixed time for the sublimate to appear.

1. A large number of antimony bearing minerals carry their antimony in the stibnite or antimonite molecule, Sb_2O_3. The mineral stibnite sublimes as Sb_4O_6 or Sb_2O_4 at 480°. Of thirteen other mineral species examined containing this molecule, the temperature of sublimation fell between 430° and 520°. Two others containing this molecule rose to 550° and 600° respectively. Both these gave up their antimony with violent deflagration, a phenomenon suggesting superheating above the normal temperature of volatilisation and oxidation. Three other minerals carrying the antimony as R_3Sb, or RSb, sublime within the limits 490—520°. The native element or the chemically purified element sublimed at 510° or a little higher.

From these results it will be inferred, contrary to what, I think, would have been expected, that a compound of the form nRS,mSb_2S_3 becomes unstable in presence of oxygen at a temperature which seems unaffected by the nature of R or the values of n or m. Thus zinkenite, PbS,Sb_2S_3, sublimes at 475°, and tetrahedrite, $4(Cu_2S),Sb_2S_3$, at the same temperature. A specimen of polybasite, $9Ag_2S,Sb_2S_3$, sublimes at 495°, &c. It would further appear that other antimony-bearing molecules besides the sesquisulphide also break up at this temperature. It is also remarkable that the temperature of sublimation may be lower than that of the free element, although I think we must conclude that it is the temperature of sublimation of this last which is the controlling factor throughout.

2. The difference between the behaviour of arsenic and antimony as volatile constituents of the molecule is interesting. The sublimation of arsenic from the arsenic-bearing compounds appears to be influenced by the structure of the molecule, so that these bodies fall into groups defined by very different sublimation temperatures.

(*a*) *Compounds containing the Molecules* RAs, RAsS, R_2As_3, *or* R_3As_4(?).—Eleven mineral species and seventeen specimens of minerals reputed to carry their arsenic in some one of these molecules have been examined. The temperature of earliest sublimation varied about 440°; one only dropping to 360°, and one rising to 515°, and then deflagrating violently. This group includes such minerals as arsenopyrite, FeAsS; glaucodot, (Co,Fe)AsS; leucopyrite, $FeAs,Fe_2As_3$; and a rammelsbergite or chloanthite to which an analysis on the apophorometer assigns the composition Ni_3As_4. (This requires confirmation).

(*b*) *Compounds containing the Molecules* As_2S_3 *or* RAs_2.—Of this group nine species and eleven specimens have been examined. The sublimation temperatures varied about 220°, the limits being 190—250°. Such bodies as proustite, $3Ag_2S,As_2S_3$, and some smaltites, $(CO,Ni)As_2$, come here. Orpiment, As_2S_3, yields arsenious oxide at 220°. A result on allemontite, $SbAs_3$, would appear to place RAs_3 in this group. An observation on skutterudite, $NiAs_3$, would determine this question.

(*c*) *Compounds containing* AsS *or Loosely Attached Arsenic*.—These are all in very close agreement, yielding arsenious oxide at about 140°, the extremes being 135—150° as observed over seven species and eight specimens. The native or chemically prepared element sublimed at 145°; realgar, AsS, at 145°; and some substances of the smaltite-chloanthite-rammelsbergite section showed a sublimate at 140°. This may be due to the presence of loosely attached arsenic or possibly to the presence of the skutterudite molecule often assigned to certain of these bodies.

Among the arsenic bearing minerals it will be seen that there is traceable a fairly regular advance in stability as the volatile atom becomes more subordinate in the molecule. This general fact seems well supported; but whether this subordination is conditioned entirely by the purely numerical ratio of the atoms in the molecule or whether the atomic weights have an influence there are not enough observations to discriminate with certainty. Again, differences in chemical affinity may well play a part. It is premature to enter into these questions. It will, however, be readily understood what use can be made of the above relations in assigning structural formulæ to complex volatile substances. Thus, arsenopyrite is written either as $FeS_2,FeAs_2$, or as FeAsS. The first of these is negatived and the second supported by the stability of the mineral over the interval 190—250°, and its decomposition within the range of group (*a*).

It is necessary to observe that a substance may, by this means of classification, be assigned to a group lower than its general formula entitles it to, if a certain amount (possibly quite small) of a less stable molecule is present. On the other hand, if it sublimes at a temperature above that proper to the reputed formula there is ground for calling the latter in question. Some analyses which I made on this basis resulted in revising the chemical formula of the substance and correcting erroneous labelling.

It is sometimes found that the sublimation cannot be completed at, or anywhere near, the group temperature, but that the rise of temperature must be carried into that of the succeeding group. A copious sublimation may then suddenly occur. This phenomenon may indicate the original presence of the molecule of the higher group, or it may result from the formation of the latter after a certain amount of the volatile element has been removed. A succession of melting-points, crystallisations, and colour changes is often noticed attending the gradual decomposition of a mineral on the apophorometer or meldometer. Either of the above explanations may apply here also. But in some cases it is easy to show that molecules of

differing stabilities must have existed constitutionally; for, if not, at each higher stage a lesser quantity of sublimate is to be expected—a geometrical decrease; whereas I have found that the successive quantities of sublimate removed may be increasing. And here I may add that a certain amount of arsenic subliming at relatively high temperatures (1000° or over), after a long interval of cessation, suggests the existence of atomic combinations whose stability places them in higher groups. It would appear justifiable to use this fractional sublimation of a substance as a means of assisting the determination of a constitutional formula.

3. The tellurides examined have, for lack of material, been few in number. Tellurium, as I showed in my first paper (*loc. cit.*), comes off as a low-temperature black sublimate of TeO, or as a high-temperature white sublimate of TeO_2. Now I have found that two tellurides of the formula RTe gave no black sublimate, but only the white at a temperature of from 800° to 900°; and five tellurides having the formula RTe_2 gave the black sublimate at 460—545°, and the white sublimate at 750—900°. Tellurium itself gave a black sublimate at about 500°, and a white sublimate at 850. According to these few observations the tellurides appear capable of grouping in somewhat the same manner as the arsenides.

Whether further experiment will enable the antimony-bearing substances to be separated into temperature-groups remains to be seen; but on the available results the difference of behaviour of the three volatile elements is remarkable, especially when considered in conjunction with the physical properties of the elements themselves. Other questions of interest suggest themselves: Will the artificial alloys reveal temperature grouping according to their atomic proportions? If my conclusions are sustained, the quantitative estimation of sublimates and observation of their temperatures of evolution will, I believe, be found useful in approaching questions of atomic stability in certain cases and in discriminating among constitutional formulæ arising from analysis.

Iveagh Geological Laboratory,
May 3, 1913.

AN IMPROVEMENT IN GAS THERMO-REGULATORS.

By A. WHITAKER.

A SERIOUS difficulty which has been encountered in designing gas thermo-regulators is the peculiar properties of a glass mercury contact. When such is introduced as the "cut off" in the instrument the mercury tends to seal externally rather than enter the comparatively fine orifice of the inlet tube, a greater quantity of mercury being therefore required for a given rise in level. Further, unless the tube-end is quite horizontal, the gas escapes from the elevated parts often in the form of bubbles, causing the flame to flicker. Again, except in cases where no attempt is made to use either a small orifice here or the capillary tube of the usual type, the mercury has a tendency to separate or adhere to the glass; the portion removed from action, having to be replaced, causes an elevation in the mean temperature of the bath. The interposition of rubber meets these difficulties to some extent, but introduces other disadvantages.

The following is offered as a solution:—

Unless the joint at A is very well made (that is, regular and symmetrical), the end of the capillary should be countersunk (by grinding) as flat as is compatible with its object. The regulator here described exhibited an angle of 135°. The flow of mercury is by this means considerably facilitated, and is approximately equal from all points.

The end of the inlet tube is ground internally to a cone, the edges being either sharp or slightly expanded, and brought very near to the prepared capillary. If properly arranged the width of the annular space between the ends of the two tubes is less than the diameter of the inlet tube when the mercury flows *up* this rather than *round* it. It is found quite possible to arrange this so that the mercury could invariably be raised half an inch in the tube, outside which no liquid appears. The space is, however, capable of passing sufficient gas when the temperature and therefore the mercury falls. This bevelling conforming to the meniscus of the mercury, assists materially in maintaining that form and preserving its continuity.

The quantity of mercury utilised is adjusted by the usual side tube. A fine screw working inside a large one (but

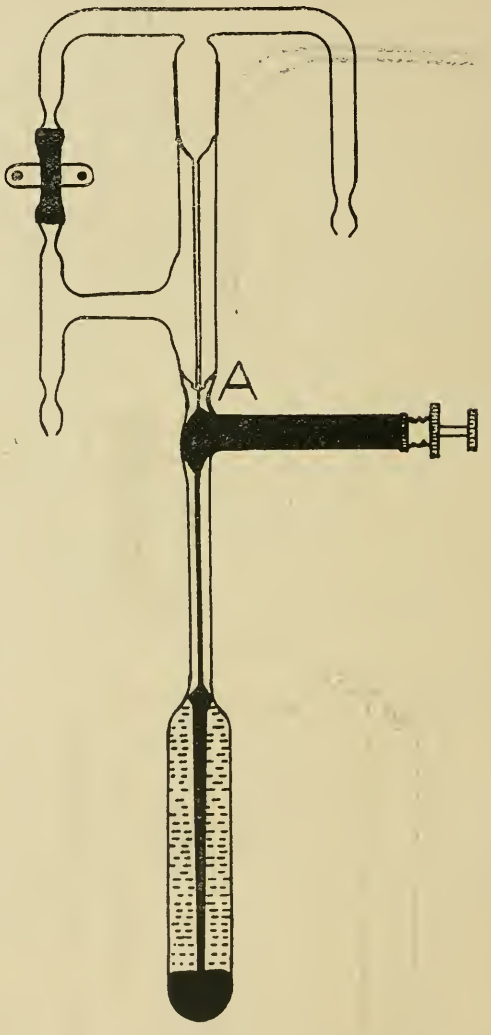


FIG. 1.

not too large) will be found more convenient than a reservoir and tap, giving considerable range with fine adjustment. This is only necessary if a large bulb be used.

The apparatus is quick in action and consequently easy of adjustment. If the bath be heated to the required temperature and the screw then turned till the flame is cut down, the mean temperature of the bath will be within a twentieth of a degree of the desired one. Half an hour is sufficient for exact adjustment, other instruments requiring occasional attention for two or three days if regulation to

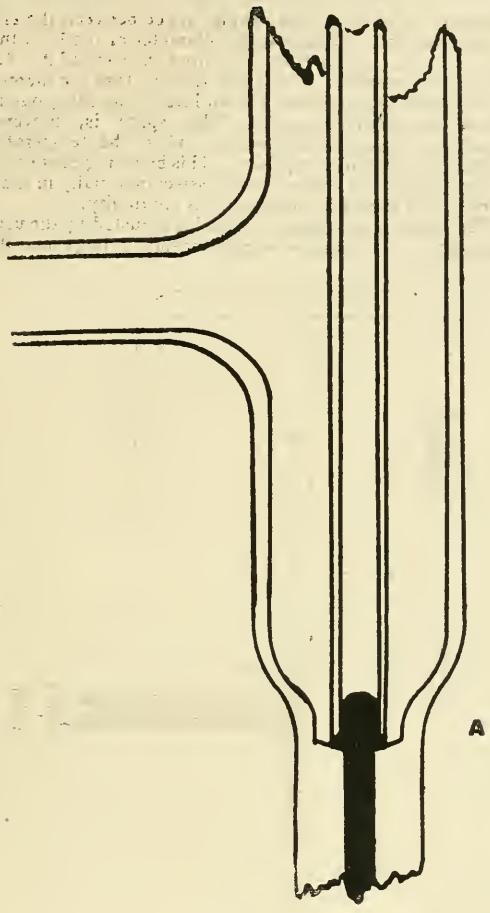


FIG. 2.

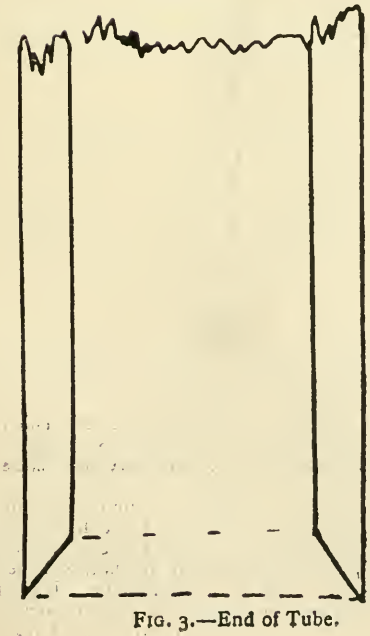


FIG. 3.—End of Tube.

a prescribed point is to be attained. It possesses great sensitiveness with quite a small sized instrument.

The one tested had a bulb 3·5 inches long and 0·5 inch diameter. It was tested in a bath holding about ten litres of water. The temperature variation with the bye-pass closed was $\pm 0{\cdot}02°$, working at 40°. A slight irregularity in the inlet tube passed a minute quantity of gas to just keep the flame alight. The bath was cooled five degrees by the addition of water, and in three quarters of an hour had regained its original temperature without rising more than 0·01° above the mean.

On opening the bye-pass (though without full adjustment) the temperature varied about 0·001° for about an hour, after which no fluctuation could be seen for the rest of the day. A Beckmann thermometer reading to a hundredth was used, the scale being sufficiently open to estimate the thousandth.

For special purposes it was required to use the instrument without any stirring arrangement. It was found to be sufficiently quick in action to prevent any fluctuation exceeding 0·1° for several days. In this case a thermometer with a very small bulb was used, capable of indicating very rapid variations.

It should be noted that for maximum sensitiveness the regulator should be clamped with the end of the inlet tube horizontal coinciding with the surface of the mercury, giving then a very sharp cut off.

The permanent adjustments, though easy with proper facilities, are somewhat difficult for the amateur glass-worker. The suggestion has therefore been placed with Messrs. A. Gallenkamp and Co. (London), from whom the apparatus may be obtained.

THE FRUIT OF THE AMERICAN HOLLY.

By F. F. CARHART and G. H. MILLER.

THIS analysis was made from the fruit of the common American holly, which is found along the entire Atlantic coast of the United States. The foliage and fruit are used a great deal for decorative purposes during the Christmas holidays. The American holly (*Ilex opaca*) is a shrub or small tree growing from ten to forty feet in height. The foliage is not as glossy nor the berries as scarlet as those of its European relative, *Ilex aquifolium*. The lower leaves are uniform, with waved spinous cartilaginous margins; the flowers are in umbellate cymes, white, and often subdioecious. The wood is white and valued by cabinet-makers for inlaying. The leaves are said to be equal to Peruvian bark for the cure of intermittent fevers. The fruit contains four bony furrowed stones. The berries are so violently purgative that five to eight berries cause violent vomiting when green. One or two of the dried berries when eaten produce nausea. The average weight of each berry was 0·1754 grm.

The Sugars.

200 grms. of the dried berries were weighed into a litre flask for the sugar extraction. They were then covered with a portion of 95 per cent alcohol. The flask was tightly fitted with an inverted condenser, and placed on a water-bath. They were treated in this manner for thirty-two or thirty-three days, the extract being removed each day and a fresh portion of alcohol added. The alcohol was separated each day by distillation and a thick syrup remained. The extract at first had a brown colour and a strong odour like fresh cider, which became more like hard cider as the extraction progressed. Toward the end of the extraction successive tests were made with Fehling's solution, which indicated that most of the sugars were out. Then distilled water was added in substitution for the alcohol in the extraction.

The berries remained hard and firm while being treated with alcohol, but on the addition of water they became

rather soft and were easily mashed. The alcoholic extract at the end of the thirty-three days was nearly clear, while at first the water extract was quite black. About fifteen days sufficed to remove all coloration and the balance of the sugars.

The amount of the sugars was determined by titration with Fehling's solution of such a strength that 10 cc. corresponded to 0·05 grm. of sugars. The determination was made by taking 1 cc. of the sugar extract and diluting with 50 cc. of distilled water in a small beaker. This was heated to boiling and titrated with Fehling's solution. To determine when the end-point was reached, a small portion of the solution was filtered from time to time, always pouring the filtrates back, until the sugars had no more reducing power. The filtrate became greenish at first and a light blue when the reduction was completed. The blue tint could be produced by three drops of Fehling's solution when the end-point was reached; and so it seemed a satisfactory test. To verify, however, we checked this result by using the method described by W. F. Sutherst in the *Journal of Industrial and Engineering Chemistry* for April, 1911, p. 256. This proved a very satisfactory test, and checked up almost exactly with the former result, which showed that we had 8·34 per cent of sugars in the water extraction, and 38·00 per cent in the alcoholic extraction, making a total of 46·34 per cent for the sugars in the dried fruit.

A portion of the sugar extract of the berries was digested for several hours on the water-bath with a relatively large amount of purified bone-black. The bone-black was removed by filtration and a portion of the filtrate was evaporated to a constant volume on a water-bath, a thick brown syrup remaining. We weighed out 0·1 grm. of this syrup and treated it with phenylhydrazine and sodium acetate according to Mulliken. The time of the osazone formation was two minutes indicating fructose and a little more than five minutes indicating glucose. As these two sugars are usually found in equal portions in berries, this result seemed satisfactory; as successive tests verified this result.

The Acids.

The acid tests were made from the sugar extracts and the only satisfactory test was that for oxalic acid.

The Ash.

Five portions of the fruit of exactly 2 grms. each were ashed in a platinum evaporating dish. From the first, silica, iron, alumina, calcium, and magnesium were determined; from the second, the sodium and potassium were removed by the J. Lawrence Smith method; from the third, the sulphates; from the fourth, the phosphates; and from the fifth, manganese and chromium were determined. The results of these analyses are as follows:—

SO_3	4·59	per cent of the ash.
Al_2O_3	10·08	,, ,,
Fe_2O_3	1·27	,, ,,
CaO	15·91	,, ,,
MgO	8·01	,, ,,
P_2O_5	14·06	,, ,,
K_2O	17·15	,, ,,
Na_2O	24·32	,, ,,
MnO	0·10	,, ,,
Cr	0·00	,, ,,
	95·49	per cent total ash.

Other portions of ash were treated likewise and the results agreed very closely. The ash was 8·31 per cent of the dried fruit.

The Proteins.

Some of the fruit was crushed and boiled in distilled water for a time. A small amount of this solution was heated with nitric acid, giving a slight yellow coloration. This changed to an orange-red when made alkaline. This shows the presence of albumen. The nitrogen was determined by the Kjeldahl method; 2 grms. of the berries gave 0·61 per cent of nitrogen.

The Oils.

The berries left from the sugar extraction, 100 grms., were used in the extraction of the oils. They were dried and then ground up in a small coffee mill. The ground berries were placed in a half-litre flask, which was tightly fitted with an inverted condenser and treated with ether. They were treated in this manner for eighty days. The oils after the ether had been distilled off were of a clear amber colour. To purify the oil it was heated for three days with ether and bone-black, using an inverted condenser. It was then filtered. By accident some of the oil was swallowed and had a very nauseating effect. The oil thickened somewhat upon standing, but with only slight heating it became thin again. It had a very distinct odour of castor-oil. The specific gravity was found to be 0·9358. It was not possible to solidify it in a freezing mixture of salt and ice. One saponification, by the method of Koetstorfer, was carried out. The equivalent was 303.

The figure shows that the oil is very nearly related to the castor-oil group. A colour test made with sulphuric acid points to castor-oil also. The physical characteristics also point to that conclusion.

The products of the saponification were separated by adding distilled water and a small quantity of ether to dissolve the unsaponifiable portion. This was separated and evaporated to constant weight. This weighed about 0·2 grm., and had the colour of a light yellow wax. It had a distinctly soapy smell. Owing to the small amount at hand no further tests could be made with this substance.

The remainder of the liquid from the saponification separation was acidified with sulphuric acid and slightly heated. Soon the fatty acids collected upon the surface of the liquid. These were separated and boiled in distilled water for several hours, then again separated from the water and dried on the water-bath. A test for acids was made and was very distinct. The acids were of a brownish hue resembling molasses. The kind of acid or acids present could not be determined with so small a quantity.

We obtained 3·005 grms. of the oil from the 200 grms. of berries, or 1·5 per cent.

Many thanks are due to Dr. N. Knight for his advice in this work.

Cornell College, May 2, 1913.

IRIDOSMINE FROM THE NEW RIETFONTEIN MINES:

Its Occurrence, Analysis, and Genesis.*

By C. BARING HORWOOD, B.Sc (Lond.), A.R.S.M., A.M.I.C.E.

(Continued from p. 234).

Genesis.

As regards the origin of these rare metals, one should remember that the atomic weights of iridium and osmium are 193 and 191 respectively (Note 10), and that the elements of highest atomic weight are, on the whole, relatively the rarest in rocks (Note 11). If one could explain why the elements of high atomic weight are rare, then as Prof. R. K. Duncan has pointed out, we should probably have the explanation of the genesis of matter (Note 12).

The forty years' work of Sir Norman Lockyer has familiarised the world with the conception of an inorganic evolution in the sun and stars, by which the heavy elements

* *Transactions of the Geological Society of South Africa*, 1912, xv, 52.

are synthesised out of the lighter ones. Sir Norman Lockyer (*Proc. Roy. Soc.*, lxi., 204), years ago, suggested a classification of the stars according to their supposed differences of temperature, and he ranged certain elements in the order of their appearance in these stars. On the other hand, the radio-active elements, radium, thorium, uranium, &c., possess the heaviest atoms known, and their radio-activity seems to depend upon their disintegration into simpler elements. It may be that the lighter elements are taking up as much energy to evolve into the heavier elements as is given up by the latter in disintegrating into the former (Note 13).

In considering the genesis of this particular occurrence of metallic elements of high atomic weight, it should be clearly borne in mind that the gold-bearing Rand bankets (Note 14) really differ *in no important essentials* from ordinary gold-bearing quartz veins; in other words, they have merely played the part of fissures, serving as channels in which mineral matter has been deposited from circulating solutions, and these channels have finally become closed to further mineralisation by the deposition of secondary silica, which is analogous to the vein quartz of an ordinary lode. In a similar manner ordinary quartz veins have become sealed by the deposition of vein quartz and other gangue material. The big diabase dykes, which occur in almost all the mines of the Rand, are abundant *and sufficient* evidence of former deep-seated communications with these channels, whence the mineralising solutions may have ascended (Note 15). Prof. J. F. Kemp (Note 16), laying special stress on the almost constant association of eruptive rocks with veins and the usually very restricted occurrence of the latter, maintains, and rightly so, that areally considered there is adequate reason to attribute to these rocks very great importance in vein production.

The iridosmine and associated metals have not been recognised *in situ* underground, nor yet in hand specimens; they are associated with the gold and pyrites; they seem mostly to occur in that auriferous banket reef known as the Carbon Leader, which is distinguished by the abundant presence of carbon, and, further, they occur with a small proportion of nickel.

The original source of nickel ores is the basic igneous rocks; these ores are usually, though not invariably, a product of differentiation of igneous magmas.

An instance is given by Messrs. Thomas and MacAlister (Note 17) of the association of iron, nickel, and carbon, with a small percentage of cobalt, occurring as a differentiation product of a basalt porphyrite on Disco Island, off the west coast of Greenland. Iron, in the form of iron pyrites, is an important constituent of the Rand bankets. The amount of iron pyrites present is probably 2 to 3 per cent (C. B. Horwood, *Trans. Geol. Soc. S.A.*, 1910, xiii., 72). Nickel and cobalt also occur in minute quantities in the bankets. (This has been proved by Mr. Andrew F. Cross, *vide* C. B. Horwood, *loc. cit.*, p. 77). The genesis of the carbon has already been traced to the basic dykes, which are so much in evidence in practically all the gold mines of the Rand (Horwood, *loc. cit.*), and which have been shown to contain appreciable amounts of carbon, iron pyrites, gold, silver (Note 18), and sometimes traces of cobalt, and it has been suggested that the gold in the bankets may be derived from the same source (Note 19).

Notes.

10. The atomic weight of gold = 197, and that of ruthenium = 102.

11. "Problems in the Geology of Ore Deposits," by Prof. J. H. L. Vogt, in the "Genesis of Ore Deposits," published by the American Institute of Mining Engineers, Second Edition (1902), p. 640.

12. "The Chemistry of Commerce, by Prof. R. K. Duncan (Harper Bros), Chap. "Rare Earths and their Application."

13. Prof. R. K. Duncan, *loc. cit.* Also Crookes on the "Genesis of the Elements," *Brit. Assoc. Report*, Birmingham, 1886. Presidential Address by Sir William Crookes, *Trans. Chem. Soc.*, 1888. "The Evolution and Devolution of the Elements," by A. C. and A. E. Jessup, *Phil. Mag.*, 1908, [6], xv., 21, and "The Elements," by Sir Wm. A. Tilden, 1910, Chap. IV. (Harper Bros.).

14. The unpayable or barren banket beds are analogous to the unpayable or barren quartz lodes, which so frequently also occur in the neighbourhood of gold-bearing quartz veins.

15. "Notes and Analyses of Typical Transvaal Rocks," by C. B. Horwood (*Trans. Geol. Soc. S.A.*, 1910, xiii., 42).

16. "Igneous Rocks and Circulating Waters as Factors in Ore Deposition," by Prof. J. F. Kemp (*Trans. Assoc. Inst. Min. Engrs.*, 1903, xxxiii., 703).

17. "The Geology of Ore Deposits" (Edward Arnold), 1909, p. 35).

18. Horwood, *loc. cit.* The presence of silver in the dykes was not discussed, but, in assaying the dyke samples, the differences between the bullion weights and the weights of fine gold consisted chiefly of silver.

19. C. B. Horwood, *loc. cit.*, p. 76; also "Notes and Analyses of Typical Transvaal Rocks," by the same author, *Trans. Geol. Soc. S.A.*, 1910, xiii., 42.

(To be continued).

THE LATEST ACHIEVEMENTS AND PROBLEMS OF THE CHEMICAL INDUSTRY.*

By CARL DUISBERG.

(Continued from p. 234).

Indanthrene and Algole Colours.

An entirely new era began for the alizarine series when Réné Bohn, in 1901, found that his new colour, indanthrene, could be used as a vat-dye for cotton. This colour can be dyed in its reduced state like indigo, but is far superior to the latter in beauty and brightness of shade, as well as in fastness to washing and light. Indeed, the fastness to light is so great that in this respect it must be termed indestructible.

On account of this phenomenal fastness, indanthrene blue caused chemists to look for other vat colours in the anthraquinone series. Their efforts did not remain unrewarded, and we already possess colours of this class giving every possible shade. The Badische Anilin and Soda Fabrik sell them under the name of "Indanthrene Colours," the Farbenfabriken vorm Friedrich Bayer and Co. under the name "Algole Colours." Chemically most of these vat colours belong to the indanthrene type; some of them are still more complicated nuclear products of the condensation of several anthraquinone molecules; others, again, are di- and tri-anthraquinonylamines. It must also be noted that to the greatest surprise of all experts in this branch, it was discovered in the laboratory of the Farbenfabriken vorm Friedrich Bayer and Co., that even some of the simplest acyl derivatives (-benzoyl) of the amino-anthraquinones are excellent vat colours.

Lake Colours.

We must not leave out of sight the importance of some colours of the aniline group and especially the anthraquinone group for the production of lakes for paints and pigment colours for wall paper. The alumina lake of alizarine, the so-called madder lake, with its fine shade and great fastness to light, is best known. Other alizarine colours also yield valuable alumina lakes; thus, alizarine sapphirole gives a blue lake of excellent fastness to light. But it is not always necessary to precipitate lakes. Some

* From the *Journal of Industrial and Engineering Chemistry*, iv., No. 10.

of the difficultly soluble vat colours may be directly employed in a finely-divided form. Thus indanthrene and algole blue already play important rôles as substitutes for ultramarine for blueing higher class paper, textiles, and even sugar.

The development of the anthracene colours, aside from the tinctorial progress, brought about remarkable results in pure chemical research; for example, the peculiar action of boric acid and the catalytic action of quicksilver in the sulphonation processes of anthraquinone.

But in this branch of our science as well there is still much room for development. Many problems remain unsolved, and new ones are continually arising. To satisfy the demand of the dyer many dyestuffs must still be synthesised.

The ceaseless efforts of the colour chemist will undoubtedly bring us farther and farther along this road, and complaints about the insufficient fastness of dyed materials will be silenced at last. If this goal is to be reached, it is absolutely necessary for the consumer to support the manufacturer, and I take this opportunity to state that in the United States of America these fast colours are to-day more generally used, and found recognition and wide-spread application here earlier than in any other country.

Pharmaceutical Chemistry.

I will now deal with the progress and problems of the pharmaceutical industry in the synthetic production of medicinal drugs. This industry is the youngest daughter of the coal-tar industry, and it is not long since she celebrated her twenty-fifth anniversary. Those who, like myself, had the good fortune to stand at her cradle when Ludwig Knorr discovered antipyrin, and to guide her first tottering steps at the time phenacetin and sulphonal were brought out, must look back with a joyful heart to this period of splendid growth. Much brilliant work has been accomplished, but a vast amount still remains to be done. Here we see chemistry and medicine intimately bound together, the one dependent upon the other, and powerless without its aid. What an organisation, what boundless intelligence is necessary, and what immense energy has to be expended in order to discover a new synthetic remedy and to smooth its path through the obstacles of commerce! First, we need a fully equipped chemical laboratory, then a pharmacological institute with a staff of men trained in medicine and chemistry, an abundance of animals to experiment upon, and finally—the latest development in this field—a chemo-therapeutic and bacteriological department, equipped according to the ideas of Prof. Ehrlich; all these must be in close connection with one another. Whatever has been evolved, and after much painstaking effort selected as useful, finds its way into the manufacturing department, there to be elaborate in the most minute details and brought to the highest possible pitch of perfection. Now begins the arduous work of the scientific department! Here the right sponsors must be found, here all prejudices must be brushed aside and an extensive propaganda initiated. Next, a host of clinicians and practitioners must be called into requisition so that what has been evolved in the silent workshop will be conducted on a staunch ship into the wide sea of publicity. And, finally, it is the calculating salesman's turn; he must bring in enough to cover all the expenses of the innumerable experiments that have been made, if the new drug, which has swallowed so much money, is to survive and prosper. Truly, all this is a task which only too often is misunderstood and insufficiently appreciated. If, however, a great hit is made—an event almost as rare as the Greek kalends—then the envious, the patent- and trademark-violator, and even the smuggler, cling to our heels and seek to rob us of our profits, which, taking everything into consideration, are really not large. But despite all this, and though unfortunately opposed by druggists and physicians even to-day, the pharmaceutical industry serenely pursues its task. For besides certain economic aims, we also have ideals to strive for. We combat systematically the symptoms of disease, and are the faithful auxiliaries both of the doctor and the harassed nurse. The agonising pains of the patient we allay with narcotics and anæsthetics. When sleep flees the couch of suffering, we compel it to return; fever, we banish. We destroy the minute organisms which cause and spread diseases. Thus we add to the store of what is valuable, and perfect what already exists. We also isolate the active principles of various drugs, and thus assure exact dosage and freedom from undesirable or even dangerous by-effects.

In the chemical works of Germany pure chemical science receives its due. In every branch of inorganic, organic, and physiological-biological chemistry we are working with an army of scientifically trained men. In synthetic chemistry, brilliant achievements have fallen to our share. Quite recently, Stolz succeeded in building up adrenalin, Decker in making hydrastinin, and Emil Fischer and Wilhelm Traube in producing purin bases. All of these are magnificent accomplishments, and many of them have been effected in the laboratories of the industry.

(NOTE.—One kgrm. adrenalin, which is now prepared synthetically, and has been introduced under the name of "suprarenin" by the Farbwerke of Hoechst, requires for its production the adrenal glands of 40,000 oxen. This product, as well as numerous other glandular preparations, is nowadays manufactured by the large American slaughter-houses themselves).

That even yet, as at the beginning—the antifebrin period—we must trust to chance is shown by the discovery of atophan, the latest valuable antiarthritic, which is due to a fortunate accidental observation. In the subject of the old ergot problem, research work is gradually bringing more light, and makes the possibility of synthetically producing a substitute a thing of the near future. The publications on this subject show that hemostatic alkaloids possess a comparatively simple constitution. That sedatives have their place in an age when nervous disorders are so common is not to be wondered at. I need merely remind you of the new adalin which has proved exceedingly useful. Recently, Emil Fischer, the master of chemical research, to whom the pharmaceutical industry is indebted for the synthetic purin bases, viz., caffein, theobromine, and theocin, as well as the valued remedies veronal and sajodin, has succeeded, after long and fruitless labours, in elucidating the constitution of tannin, and producing it synthetically. He has thus proved that it might be possible to manufacture tanning agents of all kinds artificially, and has opened up a new and promising field for research.

Chemotherapy.

But a short while ago Ehrlich drew attention to another promising branch of pharmaceutical-medical chemistry, viz., the treatment of infectious diseases by chemical means. After many years' arduous labour and many thousand experiments on different animals, this master of medicine and chemistry succeeded in demonstrating that it is possible to produce chemical substances which will kill the parasites in the human body without injuring their host, and that this action is a function of the chemical constitution. The new science, with its magical bullets directed only against the injurious organisms in the body but not affecting its cells, pursued its course from amino-phenyl-arsinic acid (atoxyl) to diaminooxyarsenobenzole (salvarsan). Thus a new synthetic preparation, an arsenic compound, is added to the old and highly effective remedies, mercury, quinine, and salicylic acid. It is certain that we are here only at the beginning of a new development. We know already that we are able to combat not only spirochetes, but also bacterial diseases, like tuberculosis. Even carcinoma and sarcoma, those growths so destructive to humanity, whose cause is, however, not yet understood, can probably be influenced in a like manner by means of selenium compounds, as first pointed out by Emil Fischer. But were we to learn to cure diseases due to trypanosomes and plasmodia, what a great work we should have accomplished in the interest of humanity and social economy,

for it is in the most fruitful lands, indeed, that these diseases, malaria and sleeping sickness, are to be found, and man and beast are ruthlessly destroyed by them. Neither salvarsan nor atoxyl are of service here, and therefore other hitherto unknown remedies must be found.

While the treatment of syphilis, with its terrible consequences, is still imperfect in spite of mercury and salvarsan, let us hope that systematic laboratory experiments with the innumerable products chemistry is able to produce from mercury and from arsenic will finally lead to complete success.

Synthetic Perfumes.

In the perfume industry the developments made since the scent of the violet was imitated with jonon, and since the successful synthesis of camphor from turpentine, are not of such nature that we need to deal with them at great length. The importance of this industry appears from its yearly turnover of 45—50 million Marks (10—12 million dollars). Here the efforts of the chemists are directed towards determining the constitution of the complex and simple natural perfumes, isolating the various products of decomposition obtained during the investigation, and finally reproducing the natural perfumes synthetically. Such results have already been achieved in the case of the odour of the rose, lily-of-the-valley, and violet. Very often certain substances are needed in the compounding of perfumes which, like indole, possess anything but a pleasant smell.

(To be continued).

SOLID OIL AS A MARINE FUEL.

The question of a solid fuel for open liners in the shape of solidified petroleum is being taken up in Europe, and the outlook for this kind of fuel seems promising according to the *Scientific American*, cvii., 326. Tests have been made in many countries with spray fuel burners, but when it came to actually applying these on shipboard an obstacle arose, as the new method would lead to a radical transformation of the existing apparatus. Besides, great storage tanks are needed for the liquid, and the action of the latter upon the walls of the tanks would be strongly felt when the vessel is rolling at sea. It was decided quite recently at a meeting of ship owners in London to go into the production of solidified petroleum brickets on a large scale. These are obtained as follows:—The crude oil is boiled and to it is added a certain amount of stearic acid with an alcoholic solution of caustic soda. Upon cooling, there is obtained a transparent mass somewhat resembling glycerin soap, and it has sufficient cohesion to allow of making it into square-shaped brickets. Such blocks have a slow and very regular combustion owing to their uniformity of structure. The weather does not seem to affect them, and they always remain clear. The heat production from them is such that a ton of solidified petroleum serves instead of 2½ tons of coal. The great saving of space on shipboard is evident, and another point is the great all-round economy realised for producing an equal amount of steam. Some British naval engineers studied the question and concluded that for a single trip of a Cunard liner from England to New York and return the lowest figure for the saving would be 60,000 dols. They also reported the following points in favour of the new fuel: —1. No appreciable modification of the furnaces or bunkers is needed. 2. The brickets burn very well in open furnaces. 3. They have a very high calorific power. 4. No inflammable gas is given off under the action of heat in the furnace. 5. They burn slowly without running of liquid, nor is there any crackling or explosion. No ash is left. 6. Their regular shape facilitates storing, and there is no space lost. 7. The brickets harden with time and reach a great crushing resistance. 8. The range of the vessel will be much increased, which is a capital point for war vessels. From another point of view, it is held that the navigation companies will be more inclined to increase the speed of the ocean liners, since they are able to obtain high steam pressure at a much less cost for fuel than before.—*Journal of Industrial and Engineering Chemistry*, iv., No. 12.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, May 1st, 1913.

Prof. W. H. Perkin, LL.D., F.R.S., President, in the Chair.

The President referred to the death, on April 10, of Mr. John Hunter, of Edinburgh, who was elected a Fellow on February 1, 1883.

Dr. J. Newton Friend was formally admitted a Fellow of the Society.

Certificates were read for the first time in favour of Messrs. Archibald Joseph Brooks, Melrose, St. Lucia, B.W.I.; Jack Cecil Drummond, B.Sc., 8, Little Heath, Old Charlton, Kent; Horace Freeman, 1535, Robson Street, Vancouver, B.C.; James Joseph Hutchinson, Cecilville, Conquer Hill, Dollymount, Co. Dublin; Marius Maxwell, 77, Lawrie Park Road, Sydenham; Percy Bernard Phillips, The London Hospital, E.; William Gilbert Saunders, 34, Hanover Street, Liverpool; Montagu George Smith, 8, Cross Road, Bromley Common, Bromley, Kent; Ebenezer Rees Thomas, M.Sc., Emmanuel College, Cambridge; John Stewart Walker, care of The Japanese Explosives Co., Ltd., Hiratsuka, Sagami. Japan; Edwin Longstaff Watson, Nawabganj, Cawnpore, India.

Of the following papers, those marked * were read:—

*119. "*Bismuthinitrites.*" By Walter Craven Ball and Harold Helling Abram.

In continuation of previous work (*Trans.*, 1905, lxxxvii., 761; 1909, xcv., 2126; 1910, xcvii., 1408) the authors have obtained and examined the following bismuthinitrites, of the formula $X_2YBi(NO_2)_6$, where X = Cs, Rb, K, (NH_4), and Tl, and Y = Ag, Li, and Na:—*Cæsium silver*, $Cs_2AgBi(NO_2)_6$; *rubidium silver*, $Rb_2AgBi(NO_2)_6$; *potassium silver*, $K_2AgBi(NO_2)_6$; *ammonium silver*, $(NH_4)_2AgBi(NO_2)_6$; *thallium silver*, $Tl_2AgBi(NO_2)_6$; *cæsium lithium*, $Cs_2LiBi(NO_2)_6$; *rubidium lithium*, $Rb_2LiBi(NO_2)_6$; *potassium lithium*, $K_2LiBi(NO_2)_6$; *ammonium lithium*, $(NH_4)_2LiBi(NO_2)_6$, H_2O; *thallium lithium*, $Tl_2LiBi(NO_2)_6$; and *thallium sodium*, $Tl_2NaBi(NO_2)_6$.

The cæsium sodium, rubidium sodium, and ammonium sodium salts have been previously described in the above mentioned papers. These salts are red, yellow, or brown, and highly crystalline. Salts containing only one metal in addition to bismuth have been obtained, in which X = Cs, Rb, or Tl (the corresponding potassium salt, $K_3Bi(NO_2)_6,H_2O$, had been described earlier; see above). These are less stable than the X_2Y salts, and crystallise in a different form.

Bismuthinitrites containing nickel, together with any of the metals represented above by X, have also been obtained. Some alkaloidal bismuthinitrites have also been examined.

*120. "*Constitution of Aliphatic Diazo-compounds.*" By Martin Onslow Forster and David Cardwell.

In the hope of distinguishing between the rival formulæ for the aliphatic diazo-compounds, the behaviour of diazocamphor and diazodeoxybenzoin towards the Grignard agents have been studied, the results being in favour of Thiele's formula. *Camphorquinone-α-methylhydrazone*, $C_{11}H_{18}ON_2$, is colourless, melts at 133—134°, and has $[\alpha]_D$ 367·5°, whilst the *β-methylhydrazone* is yellow, melts at 46°, and has $[\alpha]_D$ 296°; *benzilmethylhydrazone*, $C_{15}H_{14}ON_2$, melts at 138°.

The action of magnesium phenyl bromide on diazocamphor gives camphorquinone α-phenylhydrazone, whilst diazodeoxybenzoin is converted into a *formazyl derivative*, $C_{27}H_{22}ON_4$, accompanied by triphenylcarbinol; the substance is intensely red, melts at 152°, and when oxidised with ferric chloride yields 1 : 4 diphenyl-1 : 2 : 3 : 5-tetrazole, together with benzoic acid.

*121. "*The Influence of Temperature and Pressure on the Rate of Volatilisation of Zinc and of Cadmium.*" By THEKETH KUMARAN NAIR and THOMAS TURNER.

Practical tests show that a small residual pressure considerably raises the distillation temperature of zinc. The rate of volatilisation has therefore been determined, the method being to observe the loss with unit weight in fixed time (thirty minutes). Experiments were conducted with zinc in air, hydrogen, and carbon monoxide at selected pressures, and also with cadmium in air. Curves have been obtained showing the percentage of metal volatilised at temperatures and pressures covering a wide range.

The whole of the curves are parallel straigh lines throughout the greater portion of their length, and it is found that:—

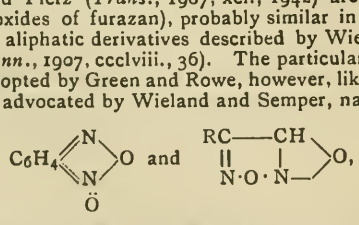
1. A certain definite temperature is required in order to give readily appreciable volatilisation.
2. This critical temperature is raised by gaseous pressure, the effect of small additions being most marked.
3. When this critical temperature has once been reached, the rate of volatilisation is independent of the initial pressure, or the nature of the gas, but it varies directly as the increase of temperature.
4. Carbon monoxide raises the initial temperature slightly less than air, and hydrogen less than carbon monoxide, although at low pressures the differences are too small to be of much practical importance.
5. The pressure temperature curve for equal rate of volatilisation is steep from 0 to 50 mm.; after an abrupt change in direction, at 50 mm., it becomes a straight line from 80 mm., and much less steeply inclined. The straight lines for zinc and cadmium in this case are not parallel.
6. The last mm. of pressure has seventy times the effect in lowering the temperature of effective distillation as compared with the removal of 1 mm. when starting from any pressure above 50 mm.

*122. "*Dinaphthathioxin and* iso*Dinaphthathioxin.*" By THOMAS JOSEPH NOLAN and SAMUEL SMILES.

It was shown that by dehydration of β-naphthol sulphide and *iso*-β-naphthol sulphide, two different naphthathioxins are respectively formed. In chemical behaviour these resemble one another very closely, but they each give rise to a distinct set of derivatives, those examined being the dichloro- and dibromo-compounds and the oxide and dioxide. It was also shown that *iso*naphthathioxin is closely related to β-naphthasulphonium-quinone. The constitution of these substances was also discussed.

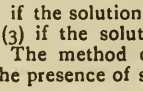
*123. "*Constitution of Furoxans (Dioxime 'Peroxides').*" By MARTIN ONSLOW FORSTER and MATTHEW FELIX BARKER.

Green and Rowe (*Trans.*, 1912, ci., 2452) have recently pointed out that the supposed dinitroso-hydrocarbons of the aromatic series, recognised as dioxime "peroxides" by Forster and Fierz (*Trans.*, 1907, xci., 1942) are actually furoxans (oxides of furazan), probably similar in constitution to the aliphatic derivatives described by Wieland and Semper (*Ann.*, 1907, cccl viii., 36). The particular oxide of furazan adopted by Green and Rowe, however, like the one previously advocated by Wieland and Semper, namely,—



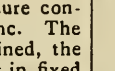
respectively, conflicts with the observation (Forster and Fierz, *loc. cit.*) that when 1 : 2-nitronaphthylazoimide and 2 : 1-nitronaphthylazoimide are heated, elimination of nitrogen leads to the same dioxime "peroxide" in each case, an origin which points unmistakably to a symmetrical constitution.

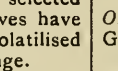
Owing to the possibility of this case being influenced by steric conditions, the present authors have inquired whether the change in question is independent of the naphthalene nucleus, and have meanwhile arrived at the conclusion that the structure of these materials may be expressed more satisfactorily by the symmetrical formula—



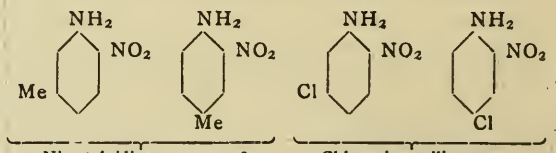
which accounts adequately for their behaviour.

124. "*Constitution of Oxadiazole Oxides (Furazan Oxides or Dioxime Peroxides).*" By ARTHUR GEORGE GREEN and FREDERICK MAURICE ROWE.

The compounds originally described as "dinitroso-compounds" were regarded later by Forster and Fierz as *o*-quinonedioximes  (*Trans.*, 1907, xci., 1942).

The new method of formation recently published by the authors (*Trans.*, 1912, ci., 2452) appeared to support the unsymmetrical structure,  , but is opposed to the observation of Forster and Fierz, that the compound $C_{10}H_6O_2N_2$ is obtained by heating either 1 : 2-nitronaphthylazoimide of 2 : 1-nitronaphthylazoimide.

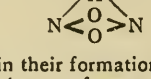
The authors have now submitted to oxidation with alkaline sodium hypochlorite the two pairs of isomerides,—



Nitrotoluidines, m. p. 109° and 114°. Chloronitroanilines, m. p. 125° and 116°.

and have found that one product is obtained from the two isomerides in each case, namely, from the first pair a methylbenzoxadiazole oxide (tolufurazan oxide) melting at 97°, and from the second pair, a chlorobenzoxadiazole oxide (chlorobenzofurazan oxide) melting at 48°.

The symmetrical structure of these substances is thus established, but in view of various objections to the dioxime-peroxide formula it is suggested that the compounds in question have the constitution—



This would explain their formation from the nitro-amines without requiring the transference of an oxygen atom from the nitro-group, and would better represent their chemical properties.

125. "*The Estimation of Zinc as Zinc Ammonium Phosphate and Zinc Pyrophosphate.*" By THOMAS MATTHEW FINDLEY and ALEXANDER CHARLES CUMMING.

The phosphate method for the estimation of zinc has been investigated in order to find the reason for occasional unsatisfactory results. It was found that the results were inaccurate (1) if the solution contained more than a trace of acetic acid; (2) if the solution, after the precipitation, was alkaline; or (3) if the solution contained sodium or potassium salts. The method can be modified to give correct results in the presence of sodium and potassium.

126. "*Condensation of Acetonedicarboxylic Acid with Phenols.*" By BIMAN BIHARI DEY.

When acetonedicarboxylic acid is condensed with α-naphthol under suitable conditions in the presence of

concentrated sulphuric acid, *methyl-α-naphthacoumarin-carboxylic acid*—

$$C_{10}H_6\!<\!\begin{matrix}O\text{———}CO\\ C(CH_2\cdot CO_2H)\end{matrix}\!>\!CH,$$

is obtained in almost quantitative yield; it melts at 214°, and on recrystallisation from boiling alcohol passes into a second modification, melting at 181·5°. These are isomeric, and when kept for some time at a few degrees above their respective melting points, give off carbon dioxide and pass into methyl-α-naphthacoumarin (Bartsch, *Ber.*, 1903, xxxvi., 1966). β-Naphthol, under similar conditions, forms the corresponding *methyl-β-naphthacoumarincarboxylic acid*, melting at 192·5°, and passing into methyl-β naphthacoumarin (m. p. 180°).

Pyrogallol, under similar treatment, yields the *compound*, $C_{11}H_8O_6$, crystallising from boiling water or alcohol in small colourless needles, melting at 215°, and passing into the compound, $C_{10}H_8O_4$ (m. p. 235°), with loss of carbon dioxide.

p-Cresol and orcinol yield the *compounds*, $C_{12}H_{10}O_4$ and $C_{12}H_{10}O_5$, melting at 185° and 262° respectively.

127. "*Oxidation of Sphingosin.*" By Arthur Lapworth.

Sphingosin, $C_{17}H_{35}O_2N$, has recently been shown to be an unsaturated dihydroxy-derivative of a primary amine (Thomas and Thierfelder, *Zeit. Phys. Chem.*, 1912, lxxvii., 511; Levene and Jacobs, *Proc. Amer. Soc. Biol. Chem.*, 1911, xxix.; *Journ. Biol. Chem.*, 1912, xi., 547).

The author finds that sphingosin, purified through the sulphate, is readily oxidised by chromic acid dissolved in glacial acetic acid, yielding pure *n*-tridecylic acid, $CH_3\cdot[CH_2]_{11}\cdot CO_2H$. The acid was identified by the usual modes of direct comparison with a specimen of *n*-tridecylic acid, prepared from α-hydroxymyristic acid, and was also converted into its α-bromo- and α-hydroxy-derivatives, which agreed in all respects with the descriptions given by Le Sueur (*Trans.*, 1905, lxxxvii., 1905).

128. "*The Conversion of Sodium Hydrosulphide into Sodium Monosulphide.*" By John Smeath Thomas and Alexander Rule.

The authors have made use of pure anhydrous sodium hydrosulphide, prepared by the action of hydrogen sulphide on sodium ethoxide (*Trans.*, 1911, xcix., 558). The reaction between sodium hydrosulphide and sodium ethoxide in alcoholic solution is reversible—

$$NaHS + C_2H_5\cdot ONa \rightleftharpoons Na_2S + C_2H_5\cdot OH,$$

and mixtures of hydrosulphide and monosulphide are obtained as products of the reaction. By increasing the concentration of sodium ethoxide, it was found possible to convert the hydrosulphide completely into the monosulphide, but the reaction does not form a suitable method for the preparation of anhydrous sodium monosulphide, owing to difficulties of separation. An alcoholate of sodium monosulphide, $Na_2S,C_2H_5\cdot OH$, was described.

The dissociation of the hydrosulphide into the monosulphide by the action of heat, according to the equation—$2NaHS = Na_2S + H_2S$, is complicated by a secondary reaction owing to the dissociation, in turn, of hydrogen sulphide, and the action of the sulphur so produced on the hydrosulphide with the formation of polysulphides. The yellow coloration which takes place when the hydrosulphide is heated above 100°, not only in air, but also in hydrogen, hydrogen sulphide, &c., is thus explained.

By heating the hydrosulphide very gradually in a vacuum, and absorbing the hydrogen sulphide evolved, the authors succeeded in bringing about the complete dissociation of the hydrosulphide into the monosulphide below 500°, without the formation of any appreciable amount of polysulphide.

129. "*Condensation of Camphorquinone with Phenols.*" By Hemendra Kumar Sen-Gupta and Biman Bihari Dey.

Camphorquinone condenses with phenol in presence of fuming hydrochloric acid to give a *compound*, $C_8H_{14}\!<\!\begin{matrix}C(C_6H_4\cdot OH)_2\\ |\\ CO\end{matrix}$, melting at 239·5°, and crystallising from glacial acetic acid in colourless, prismatic needles. The *acetyl* derivative melts at 166°, the *benzoyl* derivatives at 185°, the *dimethyl ether* at 144°, and the *dinitro*-derivative at 223°. Similar condensations have also been effected with *o*-cresol and catechol; the *o-cresol compound* melts at 241°, and yields a *dinitro*-derivative melting at 270°, a *diacetyl* derivative melting at 208°, and a *dimethyl ether* melting at 197°. The *catechol compound* crystallises from acetone in rosettes of small, colourless needles, decomposing at about 250°; the *dimethyl ether* melts at 165°.

130. "*The Interconversion of α-Hydroxy-acids and α-Ketonic Aldehydes: A Reversible Reaction.*" By Henry Drysdale Dakin and Harold Ward Dudley.

The conversion of α-ketonic aldehydes into α-hydroxy-acids by the action of alkali has long been known, and may also be effected by enzym action (*Journ. Biol. Chem.*, 1913, xiv., 155). The authors have succeeded in showing that the reverse change may take place. An aqueous solution of lactic acid, containing *p*-nitrophenyl-hydrazine, on keeping, slowly deposits methylglyoxal-dinitrophenylhydrazone, crystallising from nitrobenzene in scarlet needles, and melting and decomposing at about 300°. A similar reaction takes place with glycollic and mandelic acids—

$$R\cdot CH(OH)\cdot CO_2H \rightleftarrows R\cdot CO\cdot CHO.$$

The formation of methylglyoxal from lactic acid is of interest in connection with the relationship between lactic acid and dextrose in carbohydrate metabolism in plants and animals.

131. "*The Bacterial Oxidation of Phenol.*" By Gilbert John Fowler and Ernest Moore Mumford.

Following the work of Fowler, Ardern, and Lockett (*Proc. Roy. Soc.*, 1910, lxxxiii., B, 149), the authors have endeavoured to identify the products of fermentation and to follow the course of the reaction, when phenol is oxidised by the action of *B. helvolus*. A solution, amounting in volume to 2 litres, containing 25 parts per 100,000 of phenol, was inoculated with an active culture of *B. helvolus*, and continuously aerated for many weeks, any carbon dioxide evolved being collected in U-tubes filled with soda-lime.

Precautions were taken to prevent access of other organisms, or of carbon dioxide from the air, into the solution, to maintain a constant temperature and constant strength of solution, and to prevent moisture from entering the weighed soda-lime tubes.

The total weight of carbon dioxide evolved corresponded closely with one-sixth of the total carbon present as phenol, indicating that only one carbon atom was oxidised to carbon dioxide.

The liquid, after fermentation, was found to be faintly acid, and to give a white precipitate with baryta water. This precipitate was collected, washed with a little water, a little cold alcohol, and dissolved in boiling alcohol. From this solution a small quantity of the pure barium salt was prepared, and this, on analysis, gave Ba = 43·53, which corresponds closely with the percentage present in barium trihydroxyglutarate, namely, 43·49.

The work is being continued with the object of obtaining a larger quantity of the product of fermentation, and investigating its properties more fully.

Other phenolic derivatives are being studied by the authors and their co-workers, in the hope of arriving at a general conclusion as to the mechanism of such oxidation processes.

(To be continued).

SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS.

Ordinary Meeting, May 7th, 1913.

Mr. LEONARD ARCHBUTT, President, in the Chair.

MESSRS. Henry Francis Everard Hulton, Charles Thomas Kingzett, and Alfred James Parker were elected members of the Society.

Certificates were read for the first time in favour of Messrs. Charles William Birch, 550, Simcoe Street, Victoria, B.C.; Ulick Richardson Evans, 28, Victoria Street, Westminster, S.W.; and Harold Warren Gill, South African School of Mines and Technology, Johannesburg, S.A.

A certificate was read for the second time in favour of Mr. Frank Sturdy Sinnatt.

The following papers were read and discussed:—

"*A New Apparatus for Maintaining Constant Temperatures.*" By F. H. DUPRÉ and P. V. DUPRÉ.

The apparatus is designed so as to keep water boiling under any chosen constant pressure, the temperature of the vapour evolved being consequently also constant. Varying temperatures are obtained by altering the pressure, and the apparatus exhibited could be used to maintain temperatures between 30° C. and 145° C.

The regulation, which is entirely automatic, is very accurate, and is very nearly independent of the heat supply.

"*The Proportionate Determination of Cocoanut Oil and Palm Kernel Oil in Mixtures.*" By H. R. BURNETT and CECIL REVIS.

The relative proportion of these two fats in admixture with other fats may be ascertained with a considerable degree of accuracy, by the temperatures at which solutions in 93 per cent (by vol.) alcohol of the barium salts of the volatile water insoluble acids obtained in the Polenske process become turbid.

The results are independent of the quantity of the fats present in the original mixture.

"*The Composition of Milk.*" By H. DROOP RICHMOND.

A communication containing the results obtained during 1912.

"*Examination of the Oils from Manihot* Ceara *and* Funtumia elastica, *and a Comparison of their Properties with those of Linseed and Hevea Oils.*" By S. RIDEAL and L. H. D. ACLAND.

The authors describe the properties of the oils from the seeds of *Ceara* and *Funtumia elastica*, the rubber plants grown in the plantations of East and West Africa respectively.

The properties resemble those of the oil from *Hevea brasiliensis*, the rubber tree grown in Malay and Ceylon plantations. The oils, which belong to the drying oil class, are, in drying properties, inferior to linseed, but superior to hevea oil. Funtumia seeds, which contain a high percentage of oil, are easy to extract, and the oil is likely to find a commercial application. Funtumia oil contains 0·11 per cent of an alkaloid. Unboiled ceara seed oil gives a strong pink colouration with 2 to 3 per cent of manganese resinate.

They find that the separation of the liquid and solid fatty acids by the solubility of the potash soaps in 90 per cent acetone is useless. The liquid fatty acids were freed from ether in a vacuum containing CO_2. The values found by Hébert ("Caoutch et Guttapercha," ix., 632) for funtumia seed oil are very difficult to understand.

"*The Recovery of Iodine from Residues.*" By HAROLD W. GILL.

The author uses a solution of sodium iodide instead of potassium iodide for dissolving the iodine in iodometric estimations, since sodium iodide being soluble in absolute alcohol can, after evaporation, be recovered and used again.

NOTICES OF BOOKS.

The Chemical Constitution of the Proteins. By R. H. A. PLIMMER, D.Sc. Part II., Second Edition. London, New York, Bombay, and Calcutta: Longmans, Green, and Co. 1913.

IN the second edition of this book the author has no very startling discoveries to announce, but, on the other hand, he can report a very steady growth of our knowledge of the chemistry of the proteins. Abderhalden's remarkable analyses of the proteins and the conclusions to be drawn from his work are described in detail, as well as Osborne's investigations of the vegetable proteins and the improvements worked out by Van Slyke in methods of analysis. The use of the synthetical polypeptides in the detection and differentiation of enzymes is well explained, and recent work on the structure of the proteins is also discussed.

The Mineralogy of the Rarer Metals. By EDWARD CAHEN, A.R.C.S., F.I.C., and WILLIAM ORD WOOTTON, A.R.C.S., B.Sc. (Lond.). London: Charles Griffin and Co., Ltd. 1912.

THE widely scattered literature relating to the mineralogy and practical applications of the rarer elements has been thoroughly searched and clearly summarised by the authors of this book, which the prospector will find a valuable companion both in the field and in the laboratory. The classification of Dana is adopted, and for each mineral simple tests are given by which it may be recognised, as well as full lists of its properties and of the localities in which it has been found. A scheme for the analysis of a mineral in the field is given, and a short outline of methods of assaying some of the rarer elements. The latest available data as to the values and prices of many metals are included wherever possible. The book is well arranged and indexed, and will give the prospector valuable help in identifying minerals.

Qualitative Determination of Organic Compounds. By J. W. SHEPHERD, B.Sc. (Lond.). London: University Tutorial Press, Ltd. 1913.

BOTH the practical and educative values of a course of inorganic qualitative analysis are nowadays fully recognised, but a much less satisfactory and shorter treatment of organic analysis is generally considered sufficient for the average student. Its difficulties are undoubtedly great, but, on the other hand, it gives considerable aid in consolidating and deepening the student's knowledge of organic chemistry. In this book a successful scheme is worked out, resembling that used in inorganic work. The first part describes the reactions of the chief groups of organic substances, and gives practical details for many tests by which individual compounds may be recognised. Then follows a complete scheme for the identification of a simple substance, by subjecting it to a series of tests similar to the group and confirmatory tests in inorganic analysis. Suggestions are given for the treatment of mixtures, and for the separation of them into their constituents. In the second part different types of reactions are studied, and equations are given representing typical condensations, polymerisations, &c. The book is thoroughly practical, and will be found a valuable guide to laboratory work in organic chemistry, excluding preparations.

Die Neuere Entwicklung der Kolloidchemie. ("The More Recent Developments of Colloidal Chemistry"). By Dr. WOLFGANG OSTWALD. Dresden and Leipzig: Theodor Steinkopff. 1912. (1 Mk.).

THIS pamphlet contains the text of a lecture which was delivered before a meeting at Münster of the Deutscher

Naturforscher und Aerzte. In the short time at his disposal the lecturer gave a very striking view of the wonderful results which have been obtained by the study of colloidal chemistry, more particularly in the last six years, and probably no better short summary of the work that has been done and of the present position of our knowledge is to be found in literature. Dr. Ostwald made an excellent choice of the material he put before his audience from the great and almost bewildering abundance at his disposal, and contrived to include a comparatively full account of the experimental results which have been obtained, giving also an outline of the applications of colloidal chemistry in the industries.

Die Elektrolytische Alkalichloridzerlegung mit Festen Kathodenmetallen. ("The Electrolytic Decomposition of Alkali Chlorides with Solid Metallic Cathodes"). Part II. By Dr. Jean Billiter. Halle-a-S.: Wilhelm Knapp. 1912. (M. 9.60).

The second volume of this monograph deals with different types of cells and of plant used in the decomposition of alkali chlorides by electrolysis, and describes their arrangement and working and the results obtained with them. The Griesheim Elektron Anlage is selected for specially full treatment, and an able article from the pen of Dr. B. Scheid gives a very detailed account of it. Otherwise the various processes are described in outline only, and no theoretical discussions are introduced into the text. All who are familiar with Dr. Billiter's books on electrochemistry will recognise the thoroughness and attention to detail which is so characteristic of his work, and technologists will be grateful to him for his admirably concise and skilful handling of his subject.

CORRESPONDENCE.

EIGHTH INTERNATIONAL CONGRESS OF APPLIED CHEMISTRY, U.S.A., September, 1912.

To the Editor of the Chemical News.

Sir,—There seems a great deal of delay in the issuing of the reports of this Congress.

I should like to know if any of your readers who were members of this Congress have yet received their reports, as I myself have written to the other side several times with no definite results.—I am, &c.,

S. E. Lloyd.

61, Compton Avenue, East Ham, Essex,
May 14, 1913.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Academie des Sciences. Vol. clvi., No. 7, February 17, 1913.

Absorption of Ultra-violet Rays by Fatty Acids and their Ethers in Aqueous and Alcoholic Solutions.—Jean Bielecki and Victor Henri.—The absorption of the ultra-violet rays is nearly the same for the fatty acids and the corresponding ethers, though the absorption by the ethers is a little greater than that of the acids. Hence in a substance of formula $C_nH_{2n+1}COOR$ the absorption is determined by the acid group, the alcoholic radical having only a slight influence. Between $\lambda = 2600$ and 2144 alcoholic solutions absorb more than aqueous solutions. An increase in the number of CH_2 groups in the acid molecule does not alter the form of the absorption curve, but produces a displacement of the absorption bands towards the red. The sodium salts of formic and acetic acids absorb much less than the acids themselves, because the latter are only very slightly ionised, while the salts are strongly ionised.

Violet Chromic Sulphates.—A. Sénéchal.—When solutions of chromic sulphate are allowed to evaporate in dry air at the ordinary temperature crystals of $Cr_2(SO_4)_3.14H_2O$ separate. From the study of the vapour tensions of the different hydrates it is found that the following hydrates exist:—$(SO_4)_3Cr_2.17H_2O$, $(SO_4)_3Cr_2.16H_2O$, $(SO_4)_3.Cr_2.15H_2O$. The study of the apparent velocities of dehydration gives the same results. The sulphate, $Cr_2(SO_4)_3.14H_2O$, is dehydrated very slowly at the ordinary temperature in a dry vacuum, and this phenomenon and the transformation of the violet into the green salt are two distinct phenomena which take place with different velocities. In the former case a very unstable violet sulphate, $Cr_2(SO_4)_3.12H_2O$, is formed.

Phenyl-α-oxycrotonic Acid.—J. Bougault.—When the substance—

$$C_6H_5.CH_2.CH_2.C(OH).CO_2H$$
$$\quad\quad\quad

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xlvi., No. 3, 1913.

Triferrocarbide, Fe_3C (Cementite).—Otto Ruff and Ewald Gersten.—Jermilow has found that the molecular heat of formation of triferrocarbide is 2·27 cal., while the value obtained by the authors is −15·1 cal. The heat of oxidation of FeO to $\frac{1}{3}Fe_3O_4$ (27·5 cal.) found by Le Chatelier has been confirmed by the authors, their value being 28·6 ± 1·8 cal. This gives for the molecular heat of formation of Fe_3C from α-iron and graphite −15·3 ± 0·2 cal. The discrepancy between this and Jermilow's value is to be ascribed to the use of higher values for the molecular heat of formation of Fe_3O_4 and FeO.

Carbides of Manganese and Nickel.—Otto Ruff and Ewald Gersten.—Manganese carbide can be prepared by saturating manganese, obtained aluminothermically, with carbon by heating for about twenty minutes in a carbon crucible at 1600° in an electrical vacuum furnace under a pressure of 20 mm. The corresponding nickel compound is very unstable. The heats of formation of the three carbides at room temperature are:—

Mn_3C	.. .. ..	+12·9 ± 2·14 cal.
Fe_3C	.. .. ..	−15·3 ± 0·2 cal.
Ni_3C	.. .. ..	−39± 10 cal.

Both manganese and iron carbides are very soft substances, and the hardness of alloys containing these substances is not caused by the hardness of the carbides themselves but by the hardness of their solid solutions.

Reduction of Tungstic Acid and the Lower Oxidation Products of Tungsten.—Oscar Olsson.—If tungstic acid is reduced with tin and hydrochloric acid at 40 60° and the dark yellowish green solution finally obtained is cooled, HCl being meanwhile passed through it, a yellowish green crystalline powder separates. This is a double chloride of trivalent tungsten chloride, and a whole series of similar compounds of formula $Me^I_3W_2Cl_9$ has been prepared. They all crystallise in thin hexagonal tablets; they are fairly stable when dry, but their solutions oxidise rapidly, tungsten acid hydrate separating. If the reduction of tungstic acid is carried out at the ordinary temperature crystals which contain tetravalent tungsten separate. Their formula appears to be K_2WOHCl_5. Their aqueous solution is deep red-violet in colour, and is less stable than those of the trivalent compounds.

Catalytic Action of Mercury in Nitrations.—R. Wolffenstein and O. Böters.—In presence of mercury nitrate nitric acid converts benzene into di- and trinitrophenol. The mercury nitrate acts catalytically, the equation being—

$$C_6H_6 + 4HNO_3 = C_6H_2(NO_2)_3.OH + 3H_2O + HNO_2.$$

Mercury addition products are formed in the intermediate stage, and again decompose under the action of excess of nitric acid.

No. 4, 1913.

Action of Carbon Dioxide on the Magnesium Compound of Fenchyl Chloride.—Gust. Komppa and S. V. Hintikka.—When carbon dioxide is led into an ethereal solution of magnesium fenchyl chloride hydrofenchene carboxyllic acid, $C_{10}H_{17}.CO_2H$, which has not been prepared before, separates in glittering leaflets. It is optically inactive. Hydrodifenchen and hydrodifenchene carboxyllic acid are formed as by-products, as well as a considerable amount of fenchene, and possibly some fenchyl alcohol.

Reactions between Ferrous Oxide and Carbon and between Carbon Monoxide and Iron.—V. Falcke.—In the course of his experiments on the equilibrium constants in the system with the solid phases FeO, Fe, and C, and the gas phases CO, CO_2, the author has shown that in the equilibrium determined by Shenck, which were said to be dependent on the different modifications of carbon, the carbon was not present as a solid phase. It was further shown that the reaction between carbon monoxide and iron is more complicated than has been supposed.

New Oxide of Carbon, $C_{12}O_9$.—Hans Meyer and Karl Steiner.—A new oxide of carbon, $C_{12}O_9$, may be prepared by the complete dehydration of mellitic acid, by heating for six hours with a large quantity of benzoyl chloride. If attempts are made to dehydrate mellitic acid by the usual methods it is either quite unattacked, or else it yields a dicarboxyllic acid, $C_{12}H_2O_{10}$. The new compound may be re-crystallised from benzoyl chloride. With other solvents of high boiling points it yields characteristic colorations, *e.g.*, red with naphthalene, blue-green with nitrobenzene. It is quite insoluble in cold water, but yields mellitic acid with warm water. It may be dried at 160° without undergoing any alteration. Above 320° it darkens, and on further heating glows and burns with a dark red flame. It sublimes *in vacuo*.

MISCELLANEOUS.

Royal Institution.—Prof. Bateson's postponed lectures on "The Heredity of Sex and some Cognate Problems" will be delivered at the Royal Institution on Monday, June 2, and Wednesday, June 4, at 3 o'clock.

Electrical Resistance of Mercury.—A. Baltruszajtis.—At the melting-point the ratio,—

$$\frac{\text{Resistance of liquid mercury}}{\text{Resistance of solid mercury}} = 4{\cdot}90,$$

while at 0° the ratio becomes 4·17. The author has succeeded in determining the melting-point to within 0·3°. The measurement of the resistance of solid mercury taken nearest to the melting-point was taken at −38·91°, and that of the liquid metal at −38·11°. Within the given range of temperatures the electrical resistance of solid mercury is very nearly a linear function of the temperature. —*Butletin International de l'Academie des Sciences de Cracovie*, 1912, ix., A.

MEETINGS FOR THE WEEK.

TUESDAY, 27th.—Royal Institution, 3. "Recent Advances in the Production and Utilisation of Wheat in England," by Prof. T. B. Wood, M.A.

THURSDAY, 29th.—Royal Institution, 3. "Recent Chemical Advances —Chemistry in Space," by Prof. W. J. Pope, F.R.S., &c.

—— Royal Society. "Acineta Tuberosa—A Study on the Action of Surface Tension in Determining the Distribution of Salts in Living Matter," by A. B. Macallum. "Morphology of various Strains of the Trypanosome causing Disease in Man in Nyasaland—IV., The Mzimba Strain," by Surgeon-General Sir D. Bruce, Majors D. Harvey and A. E. Hamerton, and Lady Bruce. "Notes on *Plasma gondii*," by Helen L. M. Pixell. "Investigation by Pedigree Breeding into the Polymorphism of *Papilio polytes* (Linn.)," by J. C. F. Fryer. "Action of Radium Rays upon the Cells of Jensen's Rat Sarcoma," by S. Russ and Helen Chambers.

—— Royal Society of Arts, 4.30. "Irrigation Works in India," by Sir John Benton, K.C.I.E., &c.

FRIDAY, 30th.—Royal Institution, 9. "Parody," by Owen Seaman, M.A., &c.

—— Physical Society, 8. "Origin of New Stars," by A. W. Bickerton. "Electro-thermal Phenomena at the Contact of two Conductors with a Theory of a Class of Radio-telegraph Detectors," by W. H. Eccles. "Evaluation of certain Combinations of the Ber, Bei, and allied Functions," by S. Butterworth. "The Extraordinary Ray resulting from the Internal Reflection of an Extraordinary Ray at the Surface of an Uniaxal Crystal," by J. Walker.

SATURDAY, 31st.—Royal Institution, 3. "Radio-activity—The Origin of the β and γ-Rays and the connection between them," by Prof. E. Rutherford, F.R.S.

THE CHEMICAL NEWS.

Vol. CVII., No. 2792.

THE ESTIMATION OF PHENOL IN PRESENCE OF ORGANIC MATTER.

By E. MOORE MUMFORD.

In the course of recent bacteriological work it was found necessary to estimate small quantities of phenol, or allied bodies, in presence of comparatively large quantities of organic matter.

The phenolic solutions had been subjected to bacterial action, and contained, in addition to the phenol, which was only present in very small concentrations, comparatively large quantities of peptone, and other protein bodies. On this account the usual methods for the estimation of phenol were found to be unsuitable, and it was necessary to devise a method of estimation to suit these unusual conditions.

In the literature at the author's disposal the only methods for the estimation of phenol were :—

1. The method based on the formation of the bromine compound.

2. The method based on the complete oxidation of the phenol.

It was hardly to be hoped that either of these methods would give reliable estimations under the conditions required, and upon experiment this was found to be the case.

It was therefore necessary to devise some method by which the organic matter could be destroyed while the phenol remained to be estimated.

It occurred to the author that the well known method for the estimation of nitrates might be adapted as a method for estimating phenol.

This method is based on the principle that phenol sulphonic acid is readily nitrated, and that the resulting nitro body, on being made alkaline with ammonia, is changed to ammonium picrate, the bright yellow colour of which lends itself readily to colorimetric estimation.

The procedure was therefore inverted, the phenolic solution being first sulphonated by warming with concentrated sulphuric acid; the phenol sulphonic acid thus formed is then nitrated, and the solution boiled to destroy completely the organic matter present, the sulphonic acid, when nitrated, not being appreciably volatile in steam.

When the organic matter has thus been destroyed, the total phenol originally present in solution is still there as nitrated phenol sulphonic acid.

If the solution is now made alkaline with ammonia, the bright yellow ammonium picrate is formed.

By experiment it has been found that no appreciable quantity of phenol is lost, and that the destruction of the organic matter is sufficiently complete to prevent it interfering with the yellow colour of the ammonium picrate. The actual details of the method are as follows :—

A suitable volume of the phenol containing liquid is taken and warmed with a few cubic centimetres of concentrated sulphuric acid to 80° or 90° C.; if this temperature is not exceeded or maintained for more than a minute there is no loss of phenol, while this time is fully sufficient to sulphonate the phenol completely.

The next step is to nitrate it and, at the same time, to destroy the organic matter.

This is conveniently performed by running in to the warm solution a volume of 10 per cent potassium nitrate solution sufficient to oxidise the organic matter present, while at the same time the phenol sulphonic acid will be nitrated.

The whole is then warmed, and if necessary boiled, to destroy the organic matter.

The boiling is continued till the liquid is straw-yellow or white in colour.

It is then cooled, and when rendered alkaline with concentrated ammonia, is matched against a standard solution of phenol-sulphonic acid which has been nitrated and made alkaline in a similar manner.

This method of estimation does not claim to be extremely accurate, but with care it will yield sufficiently accurate results for ordinary purposes, and is sensitive enough to estimate 0·0001 gr. phenol.

The method may be extended, and α- and β-naphthols and salicylic acid may also be estimated in a similar manner.

The Frankland Laboratory,
The University, Manchester.

IRIDOSMINE FROM THE NEW RIETFONTEIN MINES:

Its Occurrence, Analysis, and Genesis.*

By C. BARING HORWOOD, B.Sc (Lond.), A.R.S.M., A.M.I.C.E.

(Concluded from p. 245).

Genesis (continued).

The original home of the metals of the platinum group, often with some gold and chromite, is admittedly the ultra-basic and basic igneous rocks (Note 20), in which they usually occur as primary segregations formed by magmatic concentration, which as Vogt (Note 21) remarks clearly indicates their original presence in minute proportion in these rocks (Vogt, *loc. cit.*, p. 640).

Thus, the original home of the platinum metals in other parts of the world, and the minerals with which they are here associated, at once suggest that at the Rietfontein mines they are not an original constituent of the banket, but were introduced at a later date, their original source being the big basic dykes which are so much in evidence in these mines. The arguments in support of this may be summarised as follows :—

1. The iridosmine, and the gold with which it is associated, is crystalline, and does not show evidence of being water worn, as one would expect it to do, if it were an original constituent of the banket.

2. It is reasonable to assume that these basic dykes contain minute traces of the metals of the platinum group.

Thus Vogt (Note 21) has called attention to the original tenor in the magma of the small proportion of platinum metals which has, in recent years, been found in the segregated sulphide ores of gabbro rocks, a fact which requires the supposition that the gabbro magma originally contained them. He writes :—"Some conception of this original tenor of platinum metals may be formed from the statement that the nickeliferous pyrrhotites of Sudbury contain, according to many analyses, from 25,000 to 90,000 times as much nickel as platinum metals; while the original proportion of nickel in the gabbro magma may be set down as about 0·05 per cent. Hence on the (somewhat arbitrary) assumption that the platinum metals were concentrated from the magma to the same extent as the nickel, the magma contained, roughly, 0·000001 per cent of these metals. This figure, of course, has no pretension to accuracy, but we have at least learned that even the platinum metals are among the normal constituents of the basic eruptive rocks."

At the Rietfontein gold mines it took about six months to collect about 910 grains of the heavy concentrates, during which time 102,800 tons of ore were crushed, and over 52,500 ounces of fine gold were recovered.

From these figures it would seem that the Rietfontein pay reefs contain about 27,500 times as much gold as metals of the platinum group (Note 22). The neighbouring

* *Transactions of the Geological Society of South Africa*, 1912, xv, 52.

diabase dykes contain gold (Note 23), but there is not sufficient available data to indicate the proportion of gold in the original magma; it was probably far less than that of the nickel in the case just cited. Thus it is impossible to estimate the percentage of the platinum metals in the magma on the assumption that they were concentrated from it to the same extent as the gold. However, it is just as reasonable to assume that the diabase magma originally contained them as it is to assume (as Vogt has done) that the gabbro magma, in the Sudbury occurrence, originally contained them (see also Thomas and MacAlister, *loc. cit.*, pp. 34 and 406).

3. It is associated with nickel and chromium, and it is generally admitted that both of these, as well as the metals of the platinum group, of which the concentrates consist, are derived from the ultra-basic and basic igneous rocks (J. H. L. Vogt, *loc. cit.*, p. 640; Thomas and MacAlister, *loc. cit.*, p. 34). At the Rietfontein mines such basic rocks are well represented by strong persistent diabase dykes (Note 24), 80 to 120 feet and more in thickness, which occur throughout the entire length of the mines; that is, for a distance of nearly two miles.

4. If the reader will now refer to the table of the elements as arranged by the famous Russian chemist Mendeleeff, and preferably to the one revised by him as recently as 1904 to include all the known elements except the "rare earths," it will be observed that the characteristic metallic elements of the bankets, *i.e.*, gold, silver, iron, cobalt, copper, and nickel, together with the metals of the platinum group, *form three analogous series, all occurring in Group VIII.* in Mendeleeff's table. As shown at the beginning of this paper, the metals of the platinum group have been found at several other mines as well as at Rietfontein, and, probably, closer investigation would show that they occur, in minute quantities, more or less generally throughout the mines of the Rand, as traces of these metals are invariably found when the gold, as despatched from the Rand, is refined. It is true that copper, silver, and gold are usually considered as occurring in Series, 5, 7, and 11 respectively, under Group I. It will, however, be seen that Mendeleeff indicates their very close relationship to the three analogous series of Group VIII. by also including them, in brackets, under that group. In the first analogous series of this group are iron, cobalt, nickel. and copper. Iron is largely present in the Rand bankets, chiefly in the form of iron pyrites, which, as previously stated, occurs in quantities varying from about 2 to 3 per cent (Horwood, *loc. cit.*, p. 72). Cobalt, nickel, and copper occur in minute quantities throughout the mines of the Rand (Horwood, *loc. cit.*, p. 77). Ruthenium, rhodium, palladium, and silver form the second analogous series. Both spectroscopic analyses showed that ruthenium was largely present in the heavy concentrates from Rietfontein. The probable presence of rhodium and palladium was established by the first spectroscopic analysis. Silver occurs associated with the gold of the Rand to the extent of about 125 parts per thousand of bullion (Horwood, *loc. cit.*, p. 82). The third analogous series of this group consists of osmium, iridium, platinum, and gold. The chemical analysis and both spectroscopic analyses showed that the Rietfontein concentrates were largely composed of these first two elements. The chemical analysis disclosed the presence of platinum, and the spectroscopic investigation of the first sample had also suggested its presence. In Rand bullion gold accounts for about 875 parts per thousand.

This curious association, in the Rand bankets, of these twelve elements, agreeing, as it does, in such a striking way with their chemical association and their grouping by Mendeleeff according to their atomic weights, valencies, and other chemical properties, is too remarkable to be purely accidental, and must surely indicate a very close association between them as regards their actual genesis. If, then, as regards their occurrence on the Rand, a particular genesis be admitted for any one of them, it would seem that a similar genesis must be admitted for them all.

5. They occur associated with gold, silver, pyrites, carbon, and traces of cobalt, all of which have already been shown to occur in the adjacent diabase dykes (Horwood, *loc. cit.*). The most recent investigations point to the basic dykes as the source of the gold of the bankets (Note 25); and it has been shown that the carbon, which occurs so intimately bound up with the gold, is derived from these older (longitudinal) diabase dykes (Horwood, *loc. cit.*). It is therefore reasonable to conclude that the iridosmine and associated platinum metals come from the same source.

Conclusions.

The conclusions based on the foregoing arguments are:—Firstly, that these metals are certainly of secondary origin, and, secondly, that they occurred in minute proportions, as primary segregations formed by magmatic concentration (Vogt, *loc. cit.*, p. 640), in the basic eruptives occurring in these mines, and that by the last or pneumatolytic phase (Note 26) of eruptive activity they were extracted from the dykes by active superheated gases (Note 27). Later still, hydrothermal action probably played an important part in concentrating them in the banket reefs.

Notes.

20. Thomas and MacAlister, *loc. cit.*, p. 34; Vogt, *loc. cit.*, p. 640.

21. Vogt, "Genesis of Ore Deposits," 640, 642. Also see the following footnote on the latter page:—"It may be added here that, so far as known, all primary platinum deposits were formed by igneous fusion, and that the platinum metals are either wholly wanting, or only exist in minute traces in deposits from aqueous solution. The latter fact may be due to the small susceptibility of these metals, which are, for example, much less soluble in aqua regia than gold." (See *Zeit. Prakt. Geol.*, 1898, p. 321).

22. It must, however, be remembered that the gold recovered was obtained both from the mill and the cyanide plant. The iridosmine, &c., which was recovered was obtained only from the battery; possibly some may have passed on to the cyanide works and been lost.

23. "The Mode of Occurrence and Genesis of the Carbon in the Rand Bankets," by C. B. Horwood, *Trans. Geol. Soc. S.A.*, 1910, xiii., 76, where the origin of the gold is referred to the neighbouring diabase dykes, which are shown to contain gold, except in the oxidised zone where it has been leached out.

24. In this connection it might be mentioned that Messrs. Thomas and MacAlister (*loc. cit.*, p. 27), in reference to the differentiation in the case of *dykes*, remark that the segregated minerals are identical with those from similar magmas existing in larger masses, but that the differentiation is not often so well displayed. In the CHEMICAL NEWS, civ., 283, Mr. A. G. French describes what is claimed to be a newly discovered element which he discovered in British Columbia, and calls canadium. The metal, which is described as probably belonging to the platinum group, occurs in metallic grains, and scales along with other platinum metals in *dykes* in the granite.

25. C. B. Horwood, (*loc. cit.*). Prof. R. B. Young admits that the very close association of pyrrhotite with chlorite in the bankets indicates that the introduction of at least a considerable portion of the pyrrhotite must be attributed to the basic intrusions, and that bankets and quartzites at their contact with dykes are sometimes crowded with well-formed crystals of pyrite. He refers to the frequent association of chalcopyrite and pyrrhotite, and states that he understands, on reliable authority, that sometimes the proximity of a dyke is manifested by the appearance of a noticeable quantity of chalcopyrite, galena, and pyrrhotite in the pannings of the banket. Later, in the same paper, he states that in many instances the occurrence of pyrrhotite, chalcopyrite, sphalerite, and galena is clearly related to basic intrusions, and admits that doubtless some of the pyrite has also been derived

from the same source. He also admits the close relationship between the gold and pyrite, and that in certain instances, like that described by Truscott ("The Witwatersrand Goldfields," 1907, Third Edition, p. 111), in the Worcester Mine, a relation exists between basic intrusions and the gold contents of the banket reefs. Mr. M. Weber had just previously shown (*Trans. Geol. Soc. S.A.*, 1909, vol. xiii.) that there were some acid intrusives in the Witwatersrand system, and that they contained traces, and sometimes rather more, of gold. These are of very rare occurrence in the mines of the Rand, whereas the basic dykes are everywhere in evidence. Yet Prof. R. B. Young concludes his paper and his discussion on the origin of the gold by stating in italics that he thinks it probable that "*the acid intrusives are the original source of some of the gold*" in the Main Reef series. "Further Notes on the Auriferous Conglomerates of the Witwatersrand with a Discussion of the Origin of the Gold" (*Trans. Geol. Soc. S.A.*, 1909, vol. xii.). Inasmuch as the paper is supposed to deal with the origin of the gold in the bankets the impression is given that he inclines to the theory that the acid intrusives have played a more important part as a source of the gold than the basic dykes. In this the present writer disagrees with him, and would point out that Prof. R. B. Young's own statements and arguments indicate that the *basic dykes* are the chief source of the gold in the Rand bankets.

26. Prof. R. B. Young (*loc. cit.*) calls attention to the appreciable amount of tourmaline, of undoubtedly secondary origin, in the Rand bankets, and its close association with the gold; also to the occasional occurrence of tourmaline veins in the bankets, and to the fact that tourmaline sometimes replaces portions of the quartzites and bankets; but he does not seem to have realised the full significance of these facts as strongly suggestive of pneumatolytic action. See also Thomas and MacAlister, *loc. cit.*, chap 3.

27. For an explanation of the eruptive processes by which the heavy metals have been derived from magmas, the writer would recommend the careful study of Prof. Vogt's treatise already quoted. *Vide* also "The *Rôle* of the Igneous Rocks in the Formation of Veins," by Prof. J. F. Kemp, in "The Genesis of Ore Deposits," 1901, pp. 681 and 709 (published by the American Institute of Mining Engineers). In this paper Kemp, in illustrating the competence of igneous magmas to supply both the contents of veins and the solutions which are the common carriers of the minerals, laid special stress on the fact that igneous rocks contain the metals more abundantly than the sedimentary rocks do, and also that igneous rocks are richly provided with vapours which come up with them from great depths.

THE LATEST ACHIEVEMENTS AND PROBLEMS OF THE CHEMICAL INDUSTRY.*

By CARL DUISBERG.

(Concluded from p. 247).

Artificial Silk.

Even if doubt be expressed as to whether artificial silk (the yearly consumption of which amounts to about 7 million kilogrms.) still belongs to the chemical industry because it stands in such close relation to the textile industry, with its weaving and spinning machines, yet the raw materials needed for its production, such as nitro-cellulose, copper ammonia cellulose, and cellulose-xanthogenate, are of such importance that the chemist and engineer equally divided the responsibility in this branch of manufacture. Viscose silk from xanthogenate of cellulose, the production of which has been recently very much improved, seems to replace nitro-cellulose silk and the copper ammonia silk. This viscose silk surpasses all other artificial silks in lustre and is the cheapest to manufacture, so that the apparently simplest process of all, the copper ammonia cellulose silk, cannot compete with it any more. Among the exhibits are fine speciments of this silk from the Vereinigten Glanzstoff-fabriken of Elberfeld and their factory in Oberbruch in Dremmen, near Aix-la-Chappelle, including the various raw materials, wood, cellulose, alkali cellulose, and the cellulose-xanthogenates produced by treatment with bisulphide of carbon and the viscose solution itself.

Acetylcellulose.

Cellit Films.—From acetylcellulose soluble in aceton, called cellit, the Farbenfabriken vorm Friedrich Bayer and Co. first produced cinematograph films, but although they have the great advantage over those manufactured from nitro-cellulose of being non-inflammable, it has not been possible to introduce them generally. In all their properties the cellit films are equal to the old inflammable ones, yet the proprietors of moving picture theatres do not take them up because they fear the competition of the schools and the home where the cellit films would be largely used on account of their non-inflammability. The only help then would be such action by those in authority as to make it difficult to employ inflammable films and to facilitate the use of cellit films. There are prospects of such legislation at least in Germany, which would put an end to cinematograph fires with their great danger to life and property.

Non-Inflammable Celluloid (Cellon).

The problem of manufacturing non-inflammable celluloid by mixing cellit with suitable camphor substitutes which burn difficultly or not at all may be considered as definitely solved. Eichergrün has simplified the manufacture to an extraordinary extent by showing that certain acetyl-celluloses may be gelatinised in the same way as nitro-cellulose. As is well known, nitrocellulose with camphor in the presence of a solvent yields a so-called "Solid solution," and even in the dried state may be easily cut or formed into sticks, tubes, or threads. Cellit, when treated in exactly the same way with appropriate camphor substitutes, can be converted into "cellon," the non-inflammable substitute for celluloid. Single blocks weighing 200 lbs. are already produced on a large scale which, like celluloid, can be sawed, cut, and polished; when heated can be pressed or bent; and when subjected to steam at a high temperature can be drawn and moulded. Compared with celluloid, cellon has the advantage of being more elastic, soft, and ductile. It is therefore frequently used as a substitute for hard rubber, gutta-percha, leather, &c. Cellon, in the form of a highly viscous, syrup-like solution, may be employed for coating fabrics, wood, paper, metal, &c., with a thick enamel like, uniform, and pliable surface. Thus patent leather, artificial leather, insulators, balloon covers, &c., may be produced. In France this varnish is already employed for enamelling aeroplanes. Objects made of this novel and widely useful material are to be found among the exhibits being manufactured by the Rheinisch-Westfälische Sprengstoff Actien Gesellschaft in Cologne and the Société Industrielle de Celluloid in Paris.

Rubber.

Finally, I will refer to one of the greatest successes and yet one of the most difficult problems of the chemical industry, *viz.*, the production of synthetic rubber. I am proud of the fact that its production was successfully accomplished in the works which are under my management, and that I was able to follow every stage of this important discovery. Perhaps you would be interested to hear, although it is getting late, how the whole thing happened, especially as much that is untrue and misleading has appeared in the press during the last few weeks,

* From the *Journal of Industrial and Engineering Chemistry*, iv., No. 10.

But first a few words about natural rubber. The old world owes its knowledge of this substance to the new. This wonderful product became known in Europe shortly after Columbus discovered America. If I, coming from across the ocean, now bring you this colloid prepared there synthetically, I merely repay part of the debt which we owe America.

Hardly a generation ago, the southern part of this great American continent furnished the whole supply of the different kinds of rubber. Since then extensive plantations of rubber trees have been established in various tropical countries, and their yield has grown so enormously that the old home of wild rubber will soon be thrust into the background. This is a matter which involves many millions; consequently a very serious economical problem confronts South America.

You all know that caoutchouc is made from the milky sap of numerous species of trees and shrubs and the grotesquely formed lianas by various coagulation processes, and that this product, on being suitably treated with sulphur or sulphur compounds, *i.e.*, by vulcanisation, acquires its valuable and characteristic properties. The synthetic method took quite a different route. By breaking up the very complex molecule which rubber doubtless possesses, by pyrogenetic processes, *i.e.*, by dry distillation, a veritable maze of all kinds of gases, oils, and resins was obtained, as well as a colourless fluid resembling benzine, to which the investors gave the name "Isoprene." It was the French scientist Bouchardat who first expressed the belief that this isoprene, which is obtained in very small quantities and in an impure form by the dry distillation of caoutchouc, might be closely and intimately related to caoutchouc itself. This important question was then eagerly discussed for several decades by the scientists of all countries and opinions were sharply divided. As far back as the eighties, the Englishman Tilden claimed to have prepared artificial rubber from isoprene by treatment with hydrochloric acid. But neither Tilden nor his assistants, though they worked strenuously for years, succeeded in repeating the experiments. Moreover, numerous other investigators were unable to confirm the results. Dr. Fritz Hofmann, of the Farbenfabriken vorm Friedrich Bayer & Co., is to be regarded as the real discoverer of synthetic rubber, for, by the application of heat, he succeeded in August, 1909, in polymerising the isoprene molecules into the complex rubber molecule. Somewhat later Harries discovered independently another method of arriving at the same result. Everyone is now in a position to repeat this exceedingly simple experiment himself, but in order to confirm Hofmann's results, it is necessary to employ *pure* isoprene.

The practical value of this rubber, of which many samples are among the exhibits, has been tested by the highest authorities in this branch of the industry, while Professor Karl Harries, whose unremitting labours extending over many years prepared the soil for Hofmann's synthesis, has carefully examined the chemical constitution of the substance.

Isoprene belongs to the butadienes. It was therefore to be assumed at the start that betamethylbutadiene would not hold a peculiar and isolated position among the butadienes in general. It was argued that other members of this interesting group of hydrocarbons would yield analogous and homologous rubbers on being heated. In the synthesis of products occurring in nature, there is always a possibility of producing such variations, and our endeavours to find out whether this was true in the case of rubber were crowned with success, for to-day several representatives of the new class of caoutchoucs possessing different properties are known and are being submitted to technical tests. Exact proof of the existence of the class of isomeric and homologous caoutchoucs was also first presented by Elberfeld.

To you who hear this account and see these beautiful specimens, the matter appears very simple, intelligible, and clear. In reality, however, it was not so. The difficulties which have been overcome were great indeed, and those which still remain to be surmounted in order to produce a substance equal to Para caoutchouc in quality and capable of competing with cheap plantation rubber costing only 2 marks per kilo. are still greater. But such difficulties do not intimidate the chemist and manufacturer; on the contrary, they spur them on to further efforts. The stone is rolling, and we will see to it that it reaches its destination. The end in view is this: that artificial rubber may soon play as important a rôle in the markets of the world as does natural rubber. The consumption of rubber is simply enormous. Finished articles to the value of 3 milliard marks are manufactured every year, and the raw material from which they are made, calculated at the present market price of 12 marks per kilo., costs one milliard marks. Other tasks which the chemist has on hand shrink into insignificance compared with this gigantic problem. The laurel wreath will not adorn the brow of the wild dreamer but that of the scientist who, cool and persevering, pursues his way. The seed he sows ripens slowly, and though according to the statements in the press, all this is mere child's play and the problem has been solved, I leave it to your judgment whether this is true or not, like much that printer's ink patiently transfers to paper. I am right in the midst of this excitement. I have employed articles made of synthetic rubber, and for some time I have used automobile tires made of this material. Yet, if you ask me to answer you honestly and truly when synthetic rubber will bring the millions which prophets see in its exploitation, I must reply that I do not know. Surely not in the immediate future, although synthetic rubber will certainly appear on the market in a very short time. But I hope to live long enough to see Art triumph over Nature here also.

We are now at the end of our journey. We have flown not only over the field of Germany, but also over all other countries where the chemical industry is cultivated. We have taken a passing glance at the untiring striving for advance, the restless search for the hidden and unknown, the ceaseless efforts to acquire more technical knowledge as witnessed in the great laboratories and factories of our mighty and ever-growing industry. We shall now guide our airship into the haven whence we set out and land where our co-workers have gathered from all the countries of the earth to recount whatever progress each has achieved, and to discuss, in public and private, the problems which have been solved and those which still await solution.

This is the purpose and aim of the Congresses of Applied Chemistry, and in this way they promote directly and indirectly the interests of our industry. But they also serve another purpose—to spread far and wide knowledge of our great deeds. It is thus that they impress the importance of our science and the arts founded on it upon the public in general and especially upon those who have influence in social or official positions, so that our profession may advance equally with others, and so that the importance of the chemical industry and of those connected with it from an economic, hygienic, and social standpoint may become better and better known.

That the effulgent light of this knowledge will also be diffused by the Eighth International Congress of Applied Chemistry is assured by the magnificent organisation which our friends, the American chemists, have provided, the skilful manner in which the affair has been conducted, the hospitable reception which has been extended to us, not only by our colleagues but by the people at large, and which is still awaiting us in our tours of inspection of the flourishing industry of America, in so many respects a model for others. For Chemical Science and the Chemical Industry the following words of Schiller are beautifully descriptive: "Only the serious mind, undaunted by obstacles, can hear the murmuring of the hidden spring of Truth."

THE SCIENTIFIC WEEK.

The Longitude of Washington to be Determined by Wireless Telegraphy.

The application of wireless telegraphy to the sending of time and consequently to the determining of longitudes has now arrived at a high degree of perfection, due to work accomplished in France under the auspices of the Bureau of Longitudes.

Therefore the International Conference on Time, which sat in Paris last October, has chosen that city as headquarters of the International Bureau of Time and the Eiffel Tower as horary centre. Numerous determinations of differences of longitude have been realised successfully, notably between Paris and Brussels, Lyons, Nice, Toulouse, Algiers, Bizerte, &c. ; the possibility of an operation of the same kind between Paris and Washington appeared certain in a near future, and an understanding was arrived at on this subject between the French and American delegates.

M. Darboux, perpetual secretary of the Academy of Science, has just communicated to the Academy the results of the first experiments undertaken.

Messieurs Claude, of the Bureau of Longitudes, Driencourt, Chief Hydrographic Engineer ; Major Ferrié, of the Military Telegraphic Department, with whom were associated the distinguished American technicians, Messrs. Hill, Hall, Hough, Madison, &c., established the plan of work. The success of the operations undertaken was about certain, for the American station at Arlington had heard the horary night signals from the Eiffel Tower since the month of December.

Twelve days were consecrated to trials executed under the direction of General Bourgeois, Director of the Army Geographical Service ; Mr. Jayne, Director of the Naval Observatory of Washington ; and Mr. Bullard, Director of the Radiotelegraphic Service of the American Navy at Arlington.

In spite of the unfavourable season (March) two common astronomical evenings were obtained ; they will permit a temporary determination of the difference of longitude with a precision of about 0·05 sec.

During the night of the 28th March it was even possible to exchange a conversation between Paris and Washington. It is interesting to note that this communication in both directions, at a distance of 6000 kilometres, had never been realised previously.

The definite operations, which will extend over a period of from four to six months, will probably be begun in the month of October next, conjointly by the Observatory of Paris and the Naval Observatory of Washington.

The occasion will, perhaps, be taken advantage of to try and determine with the greatest possible precision the speed of propagation of undulations across the Atlantic. Up till now it has been admitted that this speed is equal to that of light in the air, but it is possible that a different value may be found, for the propagation of the Hertzian waves is probably produced both by air and water. This special operation will then also present a high scientific interest.

Temperature of Glaciers.

Since 1898, M. Vallot, Director of the Observatories of Mont Blanc, has been studying the value of the variations of the deep temperature of glaciers at Mont Blanc. From the observations made for more than fifteen years on the glaciers situated at an altitude of more than 4000 metres it results that the diurnal variations of temperature do not exceed a metre in depth, and that from 7·50 mins. the temperature remains fixed. That is because the layer has been reached where the annual variation caused by the seasons ceases. From these observations and from the fact of the impenetrability of the inferior layers of glaciers, M. Vallot concludes that all theories concerning their flowing out or drainage are based on the introduction and freezing again of the surface water into the deep capillary fissures, and are in contradiction with the facts observed.

Solid Alcohol.

From a chemical point of view, solid alcohol is a myth. Theoricians have not, indeed, yet found out the means of manufacturing—at an ordinary temperature, be it understood—a defined body which would be alcohol and yet would not be liquid.

Fortunately smugglers have managed to do so ; it is even one of the rare services that fraud has rendered to trade. The story is worth relating.

Some years ago an unscrupulous individual, in order to deceive more easily the Parisian Custom House officers, thought of pounding white grated soap in a mortar and mixing with an equal weight of alcohol. He thus obtained a sort of homogeneous paste, which he moulded into cakes and passed through the gates without difficulty. A simple distillation on arrival at destination, and the trick was played, which, however, soon brought its author before the police-court, where pitiless judges rewarded his cleverness by sending him to the prison of Fresnes.

But the process was taken up again, honestly this time. It was the origin of the present methods which are used in preparing solid alcohol. For convenience sake these may be classed in three categories.

The first consists in fabricating a solid soap into which alcohol is mechanically incorporated. Thus, thanks to certain simple processes, at the end of the operation a translucid substance is obtained containing 60 per cent ; that is to say, two-thirds of its weight of alcohol.

Instead of employing soap as a vehicle, the alcohol may be enriched with collodion ; the process is a little more costly than the preceding one, but it gives a more satisfactory product, because of much easier combustion and of a more engaging exterior aspect.

Generally, alcohol soaps are delivered by trade in the form of a paste enclosed in a metal box made in one piece, which can be used as a warmer, the cover of which has openings that can be regulated, so as, if need be, to act as moderator to the flame ; on the contrary, the collodions of alcohol are arranged for sale in the form of pills or ovals, almost transparent. Both soaps and collodions are, however, too costly to be practically utilisable as industrial combustibles. Their employment is restricted to applications of luxury, such, for example, as being burned in toilet-lamps as travelling spirit lamps.

It is not the same for the little bricks of sawdust impregnated with alcohol and agglutinated with coal-tar that are just now being brought out in trade at a low price, and which may turn out to be a practical combustible.

The Inscription of Horary Signals from the Eiffel Tower at about One Hundredth of a Second.

M. Albert Turpain, Professor of Physics at the Faculty of Science of Poitiers, has just begun to grapple with an extremely interesting problem : the inscription of horary Hertzian signals sent by the Eiffel Tower, and in general the registration of radio-telegrams by the Morse signals.

Wireless telegraphy, which to-day plays with distances—horary signals have recently been secured at 6500 kilometres from the issuing station of Paris—is, however, a slave to the telephone.

It is easy to understand the inconveniences of such a system, based on the imperfect sensibility of the ear and of the tactile sense.

After having made researches for more than three years, M. Turpain has now practically solved the problem of the inscription of Hertzian signals at long distances.

To obtain very distinct inscriptions M. Turpain has realised extra-sensible relays or receptors. The relays, constructed with great care, assure the reception of radio-telegrams from long distances by means of an ordinary Morse apparatus.

The instruments constructed by the learned professor constitute two types of very sensitive galvanometers, one

type of a galvanometer with elbow and a type of a galvanometer with frame.

The galvanometer with elbow is realised by stretching, in a powerful magnetic charge, a very fine thread traversed by the current that is to be studied. In this way it has been possible to inscribe certain currents of *a millionth of a micro-ampère*.

But it is not necessary to arrive at such a great precision. With threads of ten hundredths of millimetres in diameter one can realise a delicate relay offering a contact sure enough to shut off currents of 10 or 20 micro-ampères. A Morse apparatus can work on such a relay.

By placing on the frame galvanometer a little oscillographic mirror, with sides of 2 millimetres by 1 millimetre, graphic photographs of Hertzian signals can be obtained.

The application of the system discovered by M. Turpain for inscribing the horary signals will be very important for the geodesy of high precision.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, May 8th, 1913.

SIR ARCHIBALD GEIKIE, K.C.B., President, in the Chair.

PAPERS were read as follows :—

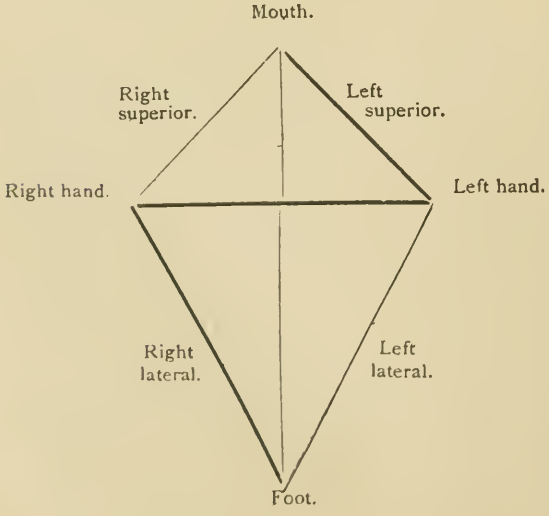
"*Various Inclinations of the Electrical Axis of the Human Heart.*" By A. D. WALLER, F.R.S.

This paper is in substance the direct continuation of a communication made to the Society in 1889 (*Phil. Trans.*, p. 162), in which it was shown (1) that the electrical effects accompanying the beat of the human heart can be demonstrated and studied by "leading off" from the mouth and from the extremities; and (2) that in consequence of the oblique situation of the heart in the thorax these "leads" are to be classified as favourable and unfavourable or strong and weak.

Of the six possible leads from the four extremities, three are strong (transverse, axial, and right lateral) and three are weak (inferior, equatorial, left lateral).

Of the four possible leads from the mouth and one extremity, one is weak (right superior) and three are strong (left superior, right and left inferior).

The five leads to be studied are represented schematically as under; the thick lines representing "strong" leads and the thin lines "weak" leads :—



The electrical equator is an imaginary line of zero potential across the chest from left shoulder to right side. The electrical current axis is from right shoulder to left side, at right angles to the equator.

The cardiac angle is the angle from the current axis with the vertical. It is calculated from the magnitudes of the systolic spike on the right and left sides by the following formulæ :—

$$\text{Sup. } \alpha \quad \tan \alpha = \frac{L - R}{L + R} \qquad \text{Inf. } \alpha \quad \tan \alpha = 2\,\frac{R - L}{R + L}$$

"*Trypanosome Diseases of Domestic Animals in Nyasaland.* III. Trypanosoma pecorum." By Surgeon-General Sir D. BRUCE, F.R.S., Majors D. HARVEY and A. E. HAMERTON, and LADY BRUCE.

"*Excystation of* Colpoda cucullus *from its Resting Cysts and the Nature and Properties of the Cyst Membranes.*" By T. GOODEY.

The ectocyst ruptures and sets free the transparent endocyst. Both ectocyst and endocyst are composed of carbohydrate substances and are resistant to acids, weak alkalis, and many other reagents; failing to give any reaction with iodine in potassium iodide solution. The endocyst is composed of a new carbohydrate for which the name *Cystose* is proposed. During excystation the endocyst wall is digested by a powerful enzyme secreted by the enclosed organism, and by this means the latter is enabled to escape. The names *Cystase* is proposed for this enzyme.

"*Experimental Hybridisation of Echinoids,*" By C. SHEARER, W. DE MORGAN, and H. M. FUCHS.

CHEMICAL SOCIETY.

Ordinary Meeting, May 1st, 1913.

Prof. W. H. PERKIN, LL.D., F.R.S., President, in the Chair.

(Concluded from p. 249).

132. "*The Vapour Pressures of Binary Mixtures.* Part II. *The Partial Pressure of Glyceryl Trinitrate in Solution in Acetone.*" By ARTHUR MARSHALL.

In Part I. (*Trans.*, 1906, lxxxix., 1350) the possible types of vapour-pressure curves were discussed and enumerated, a method of ascertaining the partial-pressure curves from the total pressure curve was described, and experimental determinations of the total pressures of various mixtures were given, amongst others those of solutions of glyceryl trinitrate (nitroglycerine) in acetone. The curve is of the type to which the author has assigned the designation Ia.

One of the peculiarities of this case is that the vapour pressure of acetone is about 160,000 times as great as that of glyceryl trinitrate, and consequently the partial-pressure curve of acetone is identical with the total pressure-curve. This, however, in no way interferes with the calculations to ascertain the form of the partial-pressure curve of glyceryl trinitrate; on the contrary, it makes the calculations somewhat easier.

The problem is of some practical importance, as it throws a light on the losses of nitroglycerine, which are liable to occur in the drying of explosives, such as cordite, which contain the two substances. It is usual nowadays to recover part of the acetone used in the manufacture of explosives by drawing air from the stoves through pipes to a suitable recovery plant. These calculations give an indication of the relative amounts of nitroglycerine, which may condense in the pipes and other parts of the plant in the different stages of the drying. Such condensation is, of course, troublesome on account of the explosibility of the substance and the special precautions that have to be adopted to deal with the condensate. The complete elucidaition of this problem would, however, also require determnations of the vapour pressures of mixtures of gun-cotton and acetone, and these are not available.

The calculations are based on Duhem's equation—

$$\frac{dp_1}{dx}\frac{x}{p_1} = -\frac{dp_2}{dx}\frac{1-x}{p_2}$$

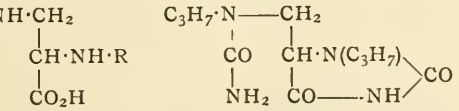
in which p and p are the two partial pressures, and x is the molecular proportion in the liquid phase of the first substance, in this case acetone. For any value of x, p can be obtained from a curve, as also can the differential dp_1/dx. The value of $p_2 \cdot dx/dp_2$ is then found by calculation, and the separate values of p_2 and dp_2/dx are obtained by a process of trial and error. The whole course of the partial-pressure curve is thus gradually ascertained.

This has been carried out for the pair of substances under consideration, with the results shown in the table below. The temperature of the measurements was 18°. At this temperature the vapour pressure of glyceryl trinitrate is estimated to be equal to about 0·001 mm. of mercury.

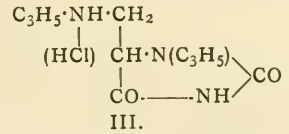
x (acetone).	p_1 (acetone).	dp_1/dx.	$p_2 \cdot 10^5$ (glyceryl trinitrate).	$-dp_2/dx \cdot 10^5$.	Glyceryl trinitrate in liquid phase, per cent.
0	0	—	100	100	100
0·1	8·2	90	89·5	109	97·2
0·2	18·4	106	78·4	113	94·0
0·3	29·5	116	67·1	113	90·1
0·4	41·5	131	55·6	117	85·4
0·5	55·7	149	43·9	117	79·7
0·6	71·3	171	31·4	113	72·3
0·7	90·0	205	20·4	108	62·6
0·8	112·2	255	10·2	93	49·4
0·9	141·0	280	3·0	72	30·3
1·0	162·0	162	0·0	—	0·0

133. "*Carbamido- and other Derivatives of αβ-Dipropylamino- and αβ-Diallylamino-propionic Acids.*" By EDWARD PERCY FRANKLAND and HENRY EDGAR SMITH.

The authors have prepared hydrobromic and nitric acid salts as well as mononitroso-derivatives of the hitherto unknown αβ-dipropylamino- and -diallylamino-propionic acids (I.). The hydrobromic acid salts were obtained in a yield of 60 and 51 per cent respectively by heating the amines with dibromopropionic acid in alcoholic solution. The dipropylamino-acid was converted into 1 : 7-dipropyltetrahydrouric acid (II.), and the diallylamino-acid into γ-allylaminomethyl-β-allylhydantoin hydrochloride (III.) by the reactions described by E. P. Frankland (*Trans.*, (1910, xcvii., 1686) in the case of the corresponding benzyl derivatives (addition of cyanic acid and dehydration with 25 per cent hydrochloric acid)—



I. II.



III.

134. "*The Relative Activities of Certain Organic Iodo-Compounds with Sodium Phenoxide in Alcoholic Solution.* Part I. *Some Normal Primary Alkyl Iodides.*" By DAVID SEGALLER.

The author has made a series of measurements of the velocity-coefficients of the interaction of the normal primary alkyl iodides and sodium phenoxide in alcoholic solution. The following homologues were dealt with :— methyl, ethyl, propyl, butyl, amyl, hexyl, heptyl, octyl, and cetyl iodides. With the exception of amyl iodide, the velocity-coefficients were found to decrease with increasing molecular weight, very rapidly from methyl to butyl iodides, and then very gradually. The coefficient for amyl iodide is very much lower than would have been expected.

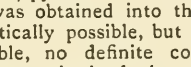
135. "*An Attempt to Resolve an Oxonium Salt.*" By STANLEY ISAAC LEVY, ERIC JOHN HOLMYARD, and SIEGFRIED RUHEMANN.

Since it has long been known that organic compounds can be obtained in which oxygen functions as a quadrivalent element, it seemed to be of interest to attempt the preparation of salts of oxonium compounds of which the molecules have no plane of symmetry, with a view to the preparation of optically active derivatives, in which the activity arises wholly or in part from the asymmetry of the oxonium group. 2-Phenyl-6-methyl-4-pyrone (Ruhemann, *Trans.*, 1908, xcviii., 431) appeared especially suitable for this purpose, since it forms a stable hydrochloride which is not hydrolysed in aqueous solution.

The hydrochloride of this base was accordingly prepared in the pure state, and treated with silver *d*-bromocamphorsulphonate.

Attempts were made to effect a resolution of the 2-phenyl-6-methyl-4-pyrone *d* α-bromocamphor-π-sulphonate which was obtained into the two forms which should be theoretically possible, but owing to the small quantities available, no definite conclusions could be drawn. The values obtained, however, indicate that interesting results should be forthcoming with larger quantities, and the authors hope to resume the work at a later date.

2-Phenyl-6-methyl-4-pyrone hydrochloride—



(*loc. cit.*, p. 434), is obtained when dry oxygen chloride is passed into a solution of the pure base in absolute ether. The faintly-yellow solid which separates is collected, and freed from ether and hydrogen chloride by being kept for several days in a vacuum over sulphuric acid and soda-lime. The compound is very readily soluble in water, alcohol, or hot acetone, crystallising from the latter in radial aggregates of needles, which, on heating, begin to soften at 125°, and melt and decompose to a dark red liquid at 165—170°.

2-Phenyl 6-methyl-4 pyrone d-*α-Bromocamphor-π-sulphonate.* $C_{12}H_{11}O_2 \cdot SO_3C_{10}H_{14}OBr$.

When the calculated quantity of silver *d*-α-bromocamphor-π-sulphonate (m. p. 145°, decomp.), dissolved in absolute alcohol, is added to a solution of the pyrone hydrochloride in the same solvent, an immediate precipitate of silver chloride is obtained. After its removal, the clear alcoholic filtrate is evaporated to dryness at 30° in a vacuum; the greyish-white residue is moderately soluble in hot acetone, from which it separates readily on cooling in colourless prisms, which begin to darken at about 90°, and melt completely to a deep red liquid at 160°—

0·2106 gave 0·4112 CO_2 and 0·0948 H_2O. C = 53·25; H = 5·00. $C_{22}H_{25}O_6SBr$ requires C = 53·12; H = 5·03 per cent.

136. "*The Spontaneous Crystallisation of Solutions of Potassium Chloride, Bromide, and Iodide.*" By BERNARD MOUAT JONES and POPATLAL GOVINDLAL SHAH.

The supersolubility curves for the solutions of potassium chloride, bromide, and iodide, and for the ice-phase in every case, have been traced, using the methods previously employed. The "metastable ranges" are about 10°, 12°, and 3° for the chloride, bromide, and iodide respectively. The vigour of the shaking was varied through a considerable range, and found to have little or no effect on the temperature of crystallisation. The rate of cooling of the tubes, so long as it was not quicker than 1° in about ten minutes, was found to have no appreciable effect on the crystallising temperature. The bearing of the work of Young (*Journ. Amer. Chem. Soc.*, 1911, xxxiii., 148) on the mechanical stimulus to crystallisation

upon the significance of the supersolubility curves was discussed.

137. "*The Absorption Spectra of some Derivatives of the Nitroaminophenols in Relation to their Constitution.*" By Raphael Meldola and John Theodore Hewitt.

The authors have examined the absorption spectra of picramic and *iso*picramic acids in alcoholic, acid, and alkaline solutions. A comparison has been instituted with 2 : 3 : 5-and 2 : 3 : 6-trinitroacetylaminoanisoles; the latter compounds, although containing no hydroxyl groups, give evidence of salt-formation with alkali of sufficient strength; this change is not accompanied by elimination of a nitro-group.

138. "*Colours Produced by Tetranitromethane with Compounds containing Elements capable of Showing Change in Valency.*" By Hans Thacher Clarke, Alexander Killen Macbeth, and Alfred Walter Stewart.

Ostromisslensky (*Journ. Prakt. Chem.*, 1911, [2], lxxxiv., 489) has shown that ethylenic compounds, when dissolved in paraffin hydrocarbons, give yellow colours with tetranitromethane. It appeared to the authors that this was probably a special case of a more general phenomenon, and experiments were therefore carried out to see if similar colorations were shown when tetranitromethane was allowed to react with compounds containing atoms of elements capable of showing a higher stage of valency. Thus, the sulphur atom in alkyl sulphides is bivalent, but is capable of becoming quadrivalent in the sulphonium compounds; and it was thought that since such an atom obviously contains a store of residual affinity, it might act in a manner similar to the unsaturated carbon atoms of ethylenic compounds. About thirty substances containing atoms of this type have been examined; and the prognostication has been found to be correct. The following results among others have been obtained.

The elements the compounds of which have been investigated are:—Bromine, iodine, nitrogen, phosphorus, sulphur, and oxygen; and in certain cases, compounds have been chosen which contained more than one atom of the elements in question.

The method employed was to dissolve the substance to be tested in chloroform (about 0·1 grm. in 5 cc.), and add to this a very dilute solution of tetranitromethane in chloroform.

It was found that the violent tint of a chloroform solution of iodine was changed to brown by the addition of tetranitromethane. There does not seem to be much of importance in this, however, as the formation of the usual brown oxonium complex would explain the occurrence of the colour without the need for any further assumptions. Ethyl iodide, on the other hand, gives a greenish yellow tint, which does not appear to be due to the presence of free iodine, as it is not removed by shaking the solution with aqueous sodium thiosulphate solution. Ethyl bromide shows no marked colour change with tetranitromethane. This is in agreement with the original hypothesis, since bromine is much less ready to produce stable compounds of higher valency than is iodine, as witness the formation of the iodonium derivatives, which have no analogues among bromine compounds.

With regard to phosphorus, it was found that triethylphosphine yields a deep yellowish brown tint. Benzyl phosphine shows a somewhat similar colour; but in this case the presence of the benzene nucleus alone might have been sufficient to bring the coloration into existence.

Taking nitrogen next, Ostromisslensky had already observed that dimethylaniline gave a dark tint with tetranitromethane. The authors have examined various groups of nitrogen derivatives. Amides, such as acetamide, formamide, and carbamide, show no colour. Amino-derivatives appear to differ from each other to some extent. Ethyl β-aminocrotonate gives a deep yellow tinge which may, however, be due to the ethylenic bond; acetaldehyde-ammonia produces a clear yellow colour, whilst urethane in alcoholic solution shows no coloration. The latter apparent anomaly may be accounted for if urethane is regarded as the amide of ethoxyformic acid. Among the cyclic nitrogen derivatives, methylpiperidine gives a golden yellow tinge.

Turning to sulphur derivatives, the following results were obtained. Alkyl sulphides show yellow tinges; propyl sulphide, for example, produces a deep golden yellow colour; whilst ethyl thiodiglycollate gives a very pale yellow. Ethylthetine shows no colour when mixed with tetranitromethane in chloroform solution; on keeping for a day or two a yellow tint is produced, but this appears to be due to tetranitromethane decomposition products. It is safe to say that under the conditions of the experiment, bivalent sulphur atoms produce a colour, whilst quadrivalent ones are inactive. Pentamethylene sulphide, in which the sulphur atom is a member of a ring, gives the same golden yellow tint as do open-chain sulphides. Thiocarbamide in alcoholic solution reacts violently with tetranitromethane, and gives a yellow colour. The origin of this reaction might be sought in the presence of traces of nitrous fumes liberated from the tetranitromethane; but no analogous reaction was observed with carbamide. Thioacetic acid shows no colour, but thioacetamide gives a pale golden yellow. Acetothienone shows a very faint discoloration.

A comparison of the results leads to an interesting point. Acetic acid and thioacetic acid show no colours, so that the conjugation of a carbonyl oxygen with a hydroxylic oxygen or a sulphur atom of the —SH group evidently has no colour-producing effect. Again, acetamide and carbamide also give no tints, so that the conjugation of carbonyl oxygen with the amide nitrogen is also not sufficient to give rise to colour. On the other hand, both thioacetamide and thiocarbamide yield yellow tints, which appears to indicate that in their case there is sufficient free residual affinity in the molecule. This agrees with the fact that sulphonium derivatives are much more stable than oxonium ones, which is probably due to the greater residual affinity of the bivalent sulphur atom.

Among the oxygen derivatives, the results at first sight appear to be anomalous. Ether, dimethylpyrone, and lactide give no colour; pentamethylene oxide gives a very faint discoloration. On the other hand, 1 : 4-dioxan shows a yellow tinge. It is clear from this that the presence of a second non-carbon atom in the six-membered ring of 1 : 4-dioxan is capable of enhancing the properties of the first one, as Clarke (*Trans.*, 1912, ci., 1788) has shown to be the case in a recent quantitative investigation.

The results for a group of six-membered cyclic substances containing all permutations of two atoms of sulphur, oxygen, and nitrogen are shown in the table below (the non-carbon atoms are placed in brackets for convenience):—

Pentamethylene oxide ..	(O)	Faint discoloration
Pentamethylene sulphide	(S)	Golden yellow
Methylpiperidine	(N)	Golden yellow
1 : 4-Dioxan	(O,O)	Pale yellow
1 : 4-Dithian	(S,S)	Lemon yellow
1 : 4-Dimethylpiperazine	(N,N)	Reddish brown
Methylmorpholine	(N,O)	Golden yellow
1 : 4-Methylthiazan . ..	(N,S)	Golden yellow
1 : 4-Thioxan	(O,S)	Lemon yellow

A comparison of these tints brings out the following:—A single etheric oxygen atom yields a practically negligible tint, but when the more highly unsaturated sulphur and nitrogen atoms are employed, marked tints are produced by the corresponding substances. Secondly, two etheric oxygen atoms, when conjugated with one another in the 1 : 4-positions in the ring, are able so to reinforce each other as to produce a colour, although a very pale one. Thirdly, when the more basic atoms of sulphur or of nitrogen are conjugated together there is produced a deepening of tinge, the reagent giving a lemon-yellow

coloration in the dithian, and brown in the dimethylpiperazine. Obviously, in these compounds, the depth of tint bears some relation to the amount of residual affinity on the atoms involved. Finally, the conjugation of a strongly basic atom, nitrogen, with a less basic one, oxygen or sulphur, produces a golden yellow colour, whereas when two weakly basic atoms, sulphur and oxygen, are conjugated, the less intense lemon-yellow tint is obtained. From these results, it appears as if this reaction might form a rough and ready way of estimating the amount of residual affinity in compounds containing atoms of this type.

A comparison of cyclic substances with the corresponding open-chain derivatives shows that very little change takes place in the tints when the ring is opened. 1 : 4-Thioxan and the corresponding open-chain compound, having the formula $MeS{\cdot}CH_2{\cdot}CH_2{\cdot}OMe$, both give lemon-yellow colours. Similarly, diphenylpiperazine gives a brown tint, whilst the open-chain analogue, $C_6H_5{\cdot}NMe{\cdot}CH_2{\cdot}CH_2{\cdot}NMe{\cdot}C_6H_5$, produces a brown tint which rapidly changes to dark green.

From the foregoing, it appears evident that the results obtained by Ostromisslensky in the case of ethylenic substances are merely a particular case of a more general phenomenon. The carbon atoms in the ethylenic bond are not fully saturated, and are therefore to be considered as analogous to those of other elements which are capable of altering their valency to a higher grade. This investigation is being continued by means of the spectrograph; and it is hoped that the results will shortly be communicated.

139. "*Note on the Oil of the Fruits of* Alpinia alba, *Rosc.*" By SAMUEL SHROWDER PICKLES and JOHN CAMPBELL EARL.

A small quantity of the fruits of *Alpinia alba*, Rosc. (*Amomum medium*, Lour.) was received at the Imperial Institute from Hong Kong in 1911. The fruits, on examination, were found to contain a volatile oil, which occurred almost entirely in the seeds.

By distilling the fruits with steam, about 1 per cent of a pale yellow oil, having an odour recalling those of lemon and eucalyptus, was obtained. The following constants were found for the oil:—$D_{15/15}$ 0·9366, α_D (in a 1-dcm. tube at 20°) $-2°15'$.

The oil, of which only 70 cc. were available, was shaken, first with dilute sodium carbonate, next with sodium hydrogen sulphite solution, then with dilute sodium hydroxide, and finally with 50 per cent resorcinol solution to absorb cineole.

From the results of this treatment and the subsequent examination of the various products, the composition of the oil was found to be approximately as follows:—

Cineole, 69 per cent; characterised by the crystalline additive product with iodol.

Aldehydes and ketones, 27·5 per cent, consisting mainly of citral, which was characterised by means of the semicarbazones and the β-naphthacinchoninic acid.

Phenols, 1·5 per cent.

Acids, 1 per cent. A small quantity of a crystalline acid, m. p. 46—48°, was isolated, but not in sufficient quantity for identification.

The residue, amounting to about 1 per cent, seemed from its odour to consist chiefly of terpenes.

PHYSICAL SOCIETY.

Ordinary Meeting, May 16th, 1913.

Prof. C. H. LEES, F.R.S., Vice-President, in the Chair.

A PAPER on "*Some Experiments to Detect β-rays from Radium* A," by Dr. W. MAKOWER and Dr. S. RUSS, was read by Dr. RUSS.

When an atom of radium A disintegrates an α particle is expelled which carries with it two positive atomic charges. At the same time the radium B atom formed recoils with a single positive charge. To account for these facts it is necessary to suppose that three negative electrons are expelled during the process. If these are emittted with a high velocity they should appear as β-rays capable of detection by the ionisation they produce or by their photographic action. On the other hand, they might consist of a slowly moving δ radiation which would escape detection by either of the above methods. The experiments, which were made by both methods in the hope of detecting β-rays from radium A, failed to reveal any such radiation.

Prof. C. H. LEES asked if Dr. Russ thought that the explanation was due to the fact that the radiations were so soft that they could not be detected.

Dr. RUSS thought that this was unlikely, as they would probably have been detected if present.

Prof. C. H. LEES remarked that as far as he could see there was no inherent improbability against the rays being so soft that they could not be detected.

A Paper on "*Dust Figures*" was read by Dr. J. ROBINSON.

The ripple formation in Kundt's tube was first satisfactorily explained by W. König in 1891. His theory was based on the hydrodynamical forces between two particles in a stream. All the known facts about these figures fall into line with the theory. The distance apart of the ripples increases with the intensity of the sound, and also from the node to the antinode there is a variation of the ripple pitch as required by the theory.

Certain measurements on dust figures produced by an electric spark have shown that these figures also can be explained in a similar way to the Kundt's tube figures.

It was suggested by Cook some years ago that viscosity must be introduced in order to account for the formation of ripples. The author shows that it is possible to account for ripple formation without introducing viscous forces at all. These will undoubtedly play some part, but more as a disturbance than as a help to the formation. In the case of the Kundt's tube figures there is a variation of velocity of the air from a node to an antinode, which produces a variation in the forces, and this causes the powder to lose its uniformity of distribution and to form ripples. The necessary constraints for the ripples are forthcoming without the introduction of viscosity.

Prof. C. H. LEES thought that Dr. Robinson's Paper filled up a gap in the subject. He had been astonished to see the magnitude of the forces that seemed to act on the grains in some of the experiments Dr. Robinson had shown him.

Prof. J. W. NICHOLSON thought Dr. Robinson's explanation was extremely convincing. He would like to know what kind of accuracy had been obtained in verifying the formula for the variation of pitch of the fringes from node to antinode, as it was deduced on the assumption that the force between any two particles was uninfluenced by the remaining ones. This correction would probably not be large in practice. The assumption that viscosity was the important factor in the phenomena was obviously untenable.

Dr. A. RUSSELL remarked that it seemed from the present Paper that the production of dust striations with an electric spark could not be regarded as proof that the discharge was oscillatory, as it often was.

Mr. F. E. SMITH asked if Dr. Robinson had ever tried to get the ripples with a light powder such as lycopodium powder. Although the force diminished very rapidly with the radius of the particles, since, in practice, the distance apart would also diminish, the actual force per unit mass acting on the particles might be about the same.

The AUTHOR, in reply to Prof. Nicholson, stated that the accuracy with which the formula was verified so surprised König that he set some of his students to measure the force between two spheres. This formula held for distances apart that were comparable to the radius of the

spheres. He did not think that the production of striations with an electric spark proved anything as to the oscillatory character of the discharge. In reply to Mr. F. E. Smith, he stated that it was quite possible to get the ripples with lycopodium powder if the intensity of the sound was kept very low. König investigated this point and showed that light powders were carried along and collected at the nodes. When this was prevented the ripples were obtained.

A paper on "*Vibration Galvanometer Design*" was read by Dr. HAWORTH.

1. The maximum amount of power available for vibrating the moving system of a vibration galvanometer of the moving-coil type is $V^2/4R$. As the frequency of the instrument is raised the losses increase rapidly, so it is an advantage to be able to increase the useful power input per unit voltage. To do this the resistance of the instrument must be decreased. This can be done in a galvanometer of the Duddell type by leading the current in and out at the bottom bridge and short-circuiting the wires at the top bridge, and it results in a great increase of sensibility. A lower resistance also requires a lower flux density.

2. Owing to the losses in the moving system increasing at a greater rate than the first power of the frequency, and that the frequency of the system increases at a slower rate than the reciprocal length of the string on account of the mass of the mirror, the flux density must be increased as the frequency increases in order that the back E.M.F. of the moving system may always be half that of the applied P.D. As the losses are low at low frequency and the mass of the mirror is not large, then, compared with the mass of the wire, the flux density required is moderate; but at high frequencies the flux density required is large. In order to obtain this result economically it is convenient to make the depth of the poles small compared with the maximum length of the wires. This gives a sufficient field for the long wires, and for short wires one is able to obtain the necessary flux density because the total flux can still be put through the moving system.

3. A combination of 1 and 2 makes a very satisfactory instrument with a much flatter voltmeter-sensibility-frequency curve than obtained usually.

Mr. W. DUDDELL remarked that the paper dealt chiefly with varying the length of the vibrating wires, but if it was required to make a really efficient galvanometer for high frequencies it was best to re-design the whole instrument, as the distance apart of the wires, the scale distance, size of mirror, &c., all ought to be altered. These various factors could be calculated beforehand, and the instrument relied upon for behaving according to the calculations. When a very low resistance was wanted silver wires could be used. He was rather afraid that sliding contacts would not be found satisfactory. It was quite true that a strong field in the centre of the wire was as good as a weak one for the whole length, but a strong field necessitated using an electromagnet, against which he had a prejudice, for vibration galvanometers. This necessitated a battery to excite it, and not only made the insulation more difficult, but also greatly increased the capacity to earth which for high frequencies it was very necessary to keep low. In his own laboratory, if he connected one terminal of a vibration galvanometer, tuned to the alternating electric light mains, to earth, he could get a very considerable deflection simply due to capacity currents. He was glad to see that Dr. Haworth had pointed out that the back E.M.F. of a vibration galvanometer behaved like a resistance since it was proportional to the applied E.M.F.

Mr. A. CAMPBELL pointed out that it was not in all cases necessary that the instrument should have as great a voltage sensitivity as possible. In some cases it was current sensitivity that was required. This depended upon the bridge the galvanometer was used with. With respect to Dr. Haworth's suggestion that the vibration galvanometer could be used as a testing machine for studying the elastic behaviour of wires, he had thought the same himself for some time, but engineers replied that it was not the properties of wires that they wanted. These had become so altered during the process of drawing as to be useless to apply to other specimens. The tests would be useful as giving the properties of wires at high frequency. In this connection he drew attention to Kapp's machine for testing materials under rapidly alternating stresses. He asked if Dr. Haworth could give any information as to how the dynamical hysteresis varied with the angle of twist. He fancied it varied as a fairly high power. He believed that nearly all the hysteresis damping was due to the bending and not to the twisting of the wires. He had had the same experience as Mr. Duddell with respect to capacity currents.

Dr. A. RUSSELL thought that a few more formulæ would have been desirable in the Paper. He remarked that the expression $V^2/4R$ for the energy absorbed was capable of very easy proof as follows:—Taking i, e, and e_b as being the instantaneous values of the current, the applied voltage and the back E.M.F., we have $i\,e_b = \frac{e_b(e-e_b)}{R}$. Taking mean values this gave $W = \frac{VV_b \cos\alpha}{R} - \frac{V_b^2}{R}$, where W was the power absorbed and V and V_b were the root mean square applied and back E.M.F.'s respectively, and α was the phase angle between them. This expression was very easily seen to give the maximum value of $\frac{V^2\cos^2\alpha}{4R}$, when $V_b = V\cos\alpha$. When adjusted for resonance cost α became unity.

The AUTHOR, in reply to Mr. Campbell, stated that he had not worked out the hysteresis law.

NOTICES OF BOOKS.

The Elements of Chemical Engineering. By T. GROSSMANN, M.A., Ph.D., F.I.C., with a Preface by Sir WILLIAM RAMSAY, K.C.B., F.R.S. Second Edition. London: Charles Griffin and Co., Ltd. 1913.

THE young chemist who has just finished his scientific training and is beginning his technical work will find that this book gives him great help in applying the knowledge he has gained in the laboratory to the very different conditions which prevail in the works. Experienced chemists will also be able to glean some hints from its lucid presentation of the main classes of problems met with in chemical engineering. In the second edition there are very few alterations, since on the whole no very striking advances have been made in the last seven years. The list of prices of chemicals has, however, been amended and brought down to date.

The Story of a Loaf of Bread. By T. B. WOOD, M.A. Cambridge: University Press. 1913.

A VERY readable and interesting account of the making of bread and of its composition is contained in this book, which is worth reading for its sketch of wheat-breeding experiments alone. The author deals first with the problems of wheat growing and marketing, and these early chapters may be commended to the farmer's careful consideration. The quality of different wheats both from the point of view of the farmer and from that of the miller is next discussed, and ways of improving the breed of the plant are explained, Mendel's theory being outlined. The author's investigation of the theory of the strength of wheat flours and his method of determining strength are described. The milling of wheat and the baking of bread are next treated, and in the final chapters on the composition of bread and different kinds of bread some

common fallacies are exposed, and recent experiments on the digestion of proteins, &c., carried out in Cambridge and in America are described.

Introduction to the Rarer Elements. By Philip E. Browning, Ph.D. Third Edition. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1912.

This book will be found an excellent if not an indispensable aid for students who are hoping to take up research work on the rarer elements. It gives complete references to the literature of the subject and includes some experimental work, both qualitative and quantitative. In the last edition the chapter on qualitative analysis has been greatly enlarged, and the complicated diagrams representing the methods of separation recently worked out by James are introduced. Much new matter has also been added to the chapter on the technical applications of the rarer elements, and tables of spectroscopic lines and plates showing typical spectra are now included.

Food Inspection and Analysis. By Albert E. Leach, S.B. Revised and Enlarged by Andrew L. Winton, Ph.D. Third Edition. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1913.

The general plan of this book is unchanged in the third edition, and it remains one of the most comprehensive text-books on food analaysis in the English language. Some obsolete matter has been omitted and its place taken by descriptions of new methods, such as processes for the detection of foreign fat in dairy products and for the determination of ammonia and acidity in meat. The use of formic acid as a preservative is discussed, and methods for its detection and determination are included. The chapters on fruit and vegetable products have been very carefully revised and new sections on dried fruits, preserves, fruit juices, &c., have been added.

Pulp and Paper. By F. P. Veitch and J. L. Merrill. Washington: Government Printing Office. 1913.

The preparation of paper, turpentine, and similar products from waste pine wood rich in rosin, is an industry which is just beginning to develop, and the authors of this bulletin have made a thorough economic and scientific study of the processes involved with a view to discovering whether it would be practicable to combine the three industries, the manufacture of paper, the distillation of wood, and the production of rosin oils. The results of their investigations of pine wood are quite satisfactory, and there appears to be no doubt that products of good quality can be obtained economically, and that the combination of the three industries is the most profitable way of using the refuse wood and stumps in the pine lands of the South and West of the United States.

Catalogue of Messrs. A. Gallenkamp and Co., Ltd., 19—21, Sun Street, Finsbury Square, London, E.C.

The above firm have recently issued a completely new catalogue containing close upon eight hundred pages and profusely illustrated. In addition to the usual chemical and physical equipment needed in the laboratory and workshops, a number of novel and recently devised pieces of apparatus are described. Centrifugal machines, mechanical shaking and stirring machines worked by hand, water motors, and electricity, Meker burners and furnaces, Jena glassware, and silica apparatus, machines for preparing and polishing metallic surfaces for microscopical examination, electric furnaces and heating apparatus, &c. The catalogue is well indexed, and is thoroughly up-to-date.

CORRESPONDENCE.

LEACH'S FOOD INSPECTION AND ANALYSIS. (Third Edition).

To the Editor of the Chemical News.

Sir,—When I observed in the first edition of this book that there was an error as to the equivalent of lactose for CuO from Fehling solution, I wrote on November 21st, 1907, to the late Mr. Leach, pointing out the fact and saying what I conceived to be the cause of the error, viz., in putting *anhydrous* in place of *crystallised* lactose (see my paper in the *Analyst*, vol. xiv., p. 82). I received a courteous reply from Mr. Leach, saying he would look into the matter.

I have now bought the third edition of the book, and find on p. 150 the same statement, that "$CuO \times 0{\cdot}6024$ gives roughly anhydrous milk sugar," with the laconic observation that "for more accurate results, however, the Defren table, p. 595, should be used." This table gives a still more erroneous result, and so I wish to caution any of my colleagues from unwarily accepting it.

By Defren's table 100 mgrms. of $CuO = 63{\cdot}2$ mgrms. of lactose, by Munson and Walker's table in the same book 100 mgrms. of $Cu_2O = 63{\cdot}0$ mgrms. of lactose. Surely the same amount of CuO and Cu_2O cannot each equal the same amount of lactose! It will be found by reference to the best authorities that the amount given in Munson and Walker's tables is the more correct.

The following are the multipliers I use for the Fehling precipitate obtained under the recognised condition and weighed as:—

		$C_{12}H_{22}O_{11}$.		$C_{12}H_{22}O_{11},OH_2$.
Cu	×	0·717	..	0·755
Cu_2O	×	0·636	..	0·670
CuO	×	0·572	..	0·602

and these are in fair agreement with all the best authorities.—I am, &c.,

E. W. T. Jones.

Wolverhampton, May 19, 1913.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clvi., No. 9, March 3, 1913.

Catalytic Method of Isomerisation of Chlorides and Bromides of Formic Acid Series.—Paul Sabatier and A. Mailhe.—Chloride and bromide of barium and chloride and bromide of thorium act catalytically to bring about the decomposition of chlorides and bromides of the formic acid series into ethylenic hydrocarbon and hydrochloric acid. These two products then re-combine, yielding not the original primary chloride, but the isomeric secondary or tertiary compound. Thus isobutyl chloride, $(CH_3)_2CHCH_2Cl$, can be transformed into the tertiary chloride, $(CH_3)_3CCl$, and isoamyl chloride, $(CH_3)_2CH.CH_2.CH_2Cl$, into the secondary chloride, $CH_3)_2CH.CHCl.CH_3$, and the tertiary chloride, $(CH_3)_2CCl.CH_2.CH_3$. The reaction is more rapid with the bromides than with the chlorides.

Action of Low Temperatures on Explosives.—André Kling and D. Florentin.—The sensitiveness of different explosives to fuses is much diminished at low temperatures, the effect of cooling being felt both by the

detonator and by the explosive itself. The force of cooled explosives does not seem to be appreciably diminished by cooling, nor the propagation of the explosion wave.

Absorption of Ultra-violet Rays by Acetylene.—Victor Henri and Marc Landau.—The ultra-violet absorption spectrum of gaseous acetylene is a fluted spectrum possessing a great number of bands. These bands can be arranged in three groups, one from $\lambda = 3157$ to $\lambda = 2880$, the next from 2800 to 2500, and the third from 2327 5 to 2236·4. Alcoholic solutions of acetylene show only one very broad absorption band, beginning at about 2850 and having a maximum at 2631.

Study of the System: Antimony Sulphide—Lead Sulphide.—H. Pélabon.—The formation of compounds of lead and antimony sulphide is not revealed by the occurrence of maxima in the temperatures of solidification, because when they fuse they decompose, but the existence of transition points and microscopic examination both reveal their formation. The formation of zincenite, Sb_2S_3PbS, and of jamesonite, $Sb_2S_3.2PbS$, is thus plainly detected.

Action of $\alpha\beta$-Dichlorethyl Oxide on Mixed Magnesium Derivatives.—MM. Lespieau and Bresch.—α-β-Dichlorethyl oxide readily attacks the magnesium derivative of acetylene, giving as the chief product a substance of formula $C_{10}H_{16}O_2Cl_2$. With bromine it gives two bromides, both corresponding to the formula $C_{10}H_{16}O_2Cl_2Br_2$. The solubilities of these two bromides are very different, and the less soluble melts at 107—108°, while the melting point of the other is 71—72°.

Methyl Magnesium Iodide.—Pierre Jolibois.—When methyl magnesium iodide is heated to 240° methane is evolved and a yellow mass of formula $Mg_2C.2MgI_2$ is left. The equation is $2[MgI_2Mg(CH_3)_2] = 3CH_4 + Mg_2C.2MgI_2$. At 600° no further evolution of gas takes place. With water the yellow compound reacts violently, nearly pure methane being evolved.

Halochromism of Derivatives of Phenylisoxazolone and of Indogenides.—André Meyer.—Certain colourless or faintly coloured organic compounds possess the power of giving coloured salts with acids, and the coloration cannot be explained by the creation of a chromphore group or a quinonic group. This phenomenon has been called halochromism. The author has found that the derivatives of phenylisoxazolone and the indogenides and their congeners also exhibit this phenomenon.

MISCELLANEOUS.

Literary Intelligence.—Messrs. J. and A. Churchill, of 7, Great Marlborough Street, W., have nearly ready an English translation of the Italian work, "A Treatise on General and Industrial Organic Chemistry," by Dr. Ettore Molinari. The work of translation has been carried out by Mr. T. H. Pope, of the School of Malting and Brewing, of the University of Birmingham. The text contains 500 illustrations.

Reduction under Pressure of Dissolved Oxygen to Hydrogen Peroxide.—Franz Fischer and Otto Priess.—The authors have constructed a steel apparatus in which a solution of oxygen in 1 per cent sulphuric acid can be electrolysed under pressure. The yields of hydrogen peroxide increase as the pressure of the oxygen is raised, and when the terminal voltage is 2 volts and the current density is 2 amps. per sq. dm., at a pressure of 100 at., 2·7 per cent peroxide solutions can be obtained, with an energy efficiency of 300—400 grms. of hydrogen peroxide per kilowatt hour (current efficiency 83 per cent). The concentration and the efficiency can be increased by employing still higher pressures.—*Ber.*, xlvi.. No. 4.

MEETINGS FOR THE WEEK.

Monday, June 2nd.—Royal Institution, 3. "The Heredity of Sex and some Cognate Problems," by Prof. W. Bateson, F.R.S., &c.

—— Society of Chemical Industry, 8. "Precipitation in Aqueous and Colloidal Systems," by W. P. Dreaper. "Some Experiments on the Theory of Electro Tanning," by E. K. Rideal and U. R. Evans. "An Illustration of the Partial Pyrite Process," by W. R. Schoeller. "Estimation of Alcohol in Beer by means of Mallig and's Ebullioscope," by J. C. Cain. "Joint Action of Catalysing Agents—Dehydration of Ethyl Alcohol and Ethyl Ether," by General W. Spatiew.

Tuesday, 3rd.—Royal Institution, 3. "Recent Advances in the Production and Utilisation of Wheat in England," by Prof. T. B. Wood, M.A.

—— Sir John Cass Institute, 5.30. "Chemistry and Technology of Hops," by A. Chaston Chapman.

Wednesday, 4th.—Royal Institution, 3. "The Heredity of Sex and some Cognate Problems," by Prof. William Bateson, F.R.S., &c.

—— Society of Public Analysts, 8. "Electrochemical Indicator for Oxidisers," by E. K. Rideal and U. R. Evans. "Estimation of Tannin in Tea," by H. L. Smith, B.Sc. "Detection and Estimation of Nickel by means of α-Benzildioxime," by F. W. Atack. "Analysis of Various East Indian Tanned Hides," by M. C. Lamb. "Sterilisation of Rag Flock Samples," by L. Reed. "General Method for the Detection of Caramel," by P. F. Thompson.

Thursday, 5th.—Royal Institution, 3. "Recent Chemical Advances —The Structure of Crystals," by Prof. W. J. Pope, F.R.S., &c.

—— Royal Society, 4.30. (The Croonian Lecture). "The Origin of Mammals," by Dr. Robert Broom.

—— Chemical, 8.30. "Relationship between the Absorption Spectra and Constitution of Piperidine, Nicotine, Cocaine, Atropine, Hyoscyamine, and Hyoscine," by J. J. Dobbie and J. J. Fox. "Equivalent Conductivities of Sodium Hyponitrite, Calcium Hyponitrite, and Hyponitrous Acid," by P. C. Ray, K. De, and N. Dhar. "Double Carbonates of the Alkaline Earth Metals and Lead with Potassium Carbonate, by R. L. Datta and H. Mukherjee. "The Estimation of Nitrites by means of Thiocarbamide, and the Interaction of Nitrous Acid and Thiocarbamide in the Presence of Acids of Different Strength," by M. E. Coade and E. A. Werner. "A Case of Isomerism in the Methylated Ferrocyanides," by E. G. J. Hartley. "Constituents of Hops," by F. B. Power, F. Tutin, and H. Rogerson. "Anomalous Rotatory Dispersion—Preliminary Note on the Form of the Dispersion-curve," by T. M. Lowry and T. W. Dickson. "Nitrogenous Constituents of Hops," by A. Chaston Chapman. "Preparation of Secondary Amines from Carboxylic Acids—Part III., Preparation of Disecondary Amines from Dicarboxylic Acids," by H. R. Le Sueur. "Guanidine Sulphocyanide, its Formation from Ammonium Sulphocyanide," by H. Krall.

Friday, 6th.—Royal Institution, 9. "Reflection and Refraction of Light as Concealing and Revealing Factors in Subaquatic Life," by Francis Ward, M.B., &c.

Saturday, 7th.—Royal Institution, 3. "Radio-activity—The Radioactive State of the Earth and Atmosphere," by Prof. E. Rutherford, F.R.S., &c.

NOTES AND QUERIES.

⁂ Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Hydrofluoric Acid.—A correspondent wishes to know where he can obtain information on the manufacture of hydrofluoric acid.—H. L. M.

Chemist, recently left College, desires Position to gain general experience.—Address, C. R., Chemical News Office, 16, Newcastle Street, Farringdon Street, London, E.C.

THE CHEMICAL NEWS.

Vol. CVII., No. 2793.

THE IDENTIFICATION OF SMALL AMOUNTS OF DYESTUFFS BY OXIDATION WITH BROMINE.

By WALTER E. MATHEWSON,
Assistant Chemist, New York Food and Drug Inspection Laboratory.

The test to aid in identifying small amounts of colouring matters, which is described in this paper, has been in use in the New York laboratory for some time. It is simple, in many cases very sensitive, and seems to require no special care to obtain reasonably dependable results.

A few cc. of the dye solution is treated with bromine water, added drop by drop until about twice as much has been used as is required to destroy the colour. Some hydrazine sulphate solution is then added to take up the excess of bromine, and finally an excess of sodium carbonate. A second test portion is treated in exactly the same way, except that a few drops of α-naphthol solution (10 per cent in 50 per cent alcohol) are added just before making alkaline with the carbonate.

The behaviour of some of the different classes of dyes may be indicated by typical examples, which show reactions obtained using 0·01 per cent solutions of the dyes unless otherwise indicated. Solutions of the natural colouring matters, however, were made by boiling 0·1 grm. of the plant or animal tissue with 100 cc. of water. The numbers after the names in the table refers to the Green-Schultz Julius tables.

With the azo-dyes, diazonium compounds are formed as shown by M. P. Schmidt (*Journ. Prakt. Chem.*, 1912, lxxxiv., 235), the azo-group in most cases remaining attached to the non-hydroxylated or -aminated residue (that of the diazo component). On addition of α-naphthol, followed by sodium carbonate, coupling takes place, and by the solubilities of the dye formed, in ether and in amyl alcohol, and by its behaviour when dyed in wool, the first component can usually be readily identified.

With some dyes, however, such as Bordeaux B and amaranth, products are formed by the oxidation which themselves react with the diazo compound, producing coloured azo-derivatives. The dye thus formed from amaranth is red in acid and blue in sodium carbonate solutions, and becomes pale brown on addition of caustic alkalis.

The monazo colours are readily attacked by bromine, the diazo colours less readily, those derived from triphenyl methane with some difficulty, and the acid fluorescein dyes merely pass more or less completely into the stable bromine derivatives. In general, the colour should be in neutral or faintly acid solution. Hydrochloric acid, however, if not present in excessive amount, in most cases does not interfere. If much foreign matter is present, the dye should be purified by taking up with amyl alcohol

Identification of Small Amounts of Colouring Matters.

Class.	Colouring matter.	Colorations obtained on addition of: Bromine.	Hydrazine sulphate.	Sodium carbonate.	α-Naphthol and sodium carbonate.
Nitro	Naphthol yellow S (4)	Colourless	Colourless	Yellowish brown	Yellowish brown
Monazo (*a*)	Tartrazin (94)	Colourless	Colourless	Colourless	Red
Monazo (*b*)	New coccin (106)	Pale yellow	Pale yellow	Very pale olive	Purplish red
	Amaranth (107)	Pale yellow	Pale brownish	Deep blue	Purplish red
	Fast red C (103)	Pale yellow	Pale brownish to pale pink	Bluish red	Purplish red
Disazo	New red L (163)	Brown	Pale brownish	Brown	Purple to brown
Triphenylmethane	Light green SF yellowish (435)	Pale brown	Nearly colourless	Nearly colourless	Nearly colourless
Xanthene	Erythrosin (517)	Brown	Brown	Red, green fluorescence	Red, green fluorescence
	Rhodamin B (504)	Precipitate	—	—	—
	Rhodamin B 0·002 per cent	Colourless, then bluish red	Bluish red	Bluish red, paler	Bluish red, paler
Alizarin	Alizarin red S (546)	Pale yellow	Yellow	Purplish red	Purplish red
Azin	Safranin (584)	Precipitate	—	—	—
	Safranin 0·002 per cent	Nearly colourless	Red	Red	Red
	Azocarmine G (604)	Pale greenish yellow	Red	Red	Red
Quinoline	Quinoline yellow	Colourless	Yellow	Yellow	Yellow
Natural colouring matters	Fustic	Deep brown, then yellow	Pale yellow	Pale brown	Pale brown
	Saffron	Colourless	Colourless	Pale yellow	Pale yellow
	Cochineal	Pale yellow	Pale yellow	Pale brown	Pale brown

Except with dyes very readily attacked where decolorisation takes place, and with a few basic colouring matters, the coloration on adding bromine is of no importance, a yellow tint being perhaps due chiefly to the excess of halogen. Chlorine water seems to give the same reactions as bromine water, but is inconvenient to prepare and offers no special advantages.

In general, it may be said that if in testing unknown solutions the dye is bleached by bromine and restored by hydrazine, or if the coloration with α-naphthol and sodium carbonate is different from that with sodium carbonate alone, a coal-tar colour is present.

THE FRUIT OF THE *SYMPHOCARPUS RACEMOSUS*, OR SNOW BERRY.

By C. B. SMITH.

THE cultivated snow-berry is a small, smooth, and much-branched shrub of the honeysuckle family, common to northern North America. It has opposite oval leaves and inconspicuous rose-coloured flowers in racemes, often leafy. While of somewhat sprawling habit, snow-berries are valuable because of their power of increasing rapidly by suckers and for their ornamental white pulpy inedible berries, borne in such abundance as to bend down the slender branches, and they are retained far into the winter. The berries used for analysis, after being dried at 100° C., lost 85 per cent of their weight. The fruit diminished so much in weight on drying that three or four seasons were required to secure the material for this study. The dried berries possessed an odour resembling that of raisins, and consisted almost entirely of a tough outer skin and two small seeds. The taste was at first sweet, followed by a slight bitterness. When burned, they first gave off a burnt sugar odour, followed by the odour characteristic of burning leaves. The average weight of each berry when picked was 0·5 grm.; when dried 0·088 grm.

The Ash.

Five different portions of the berries of about 2 grms. each were ashed in a platinum evaporating dish of 100 cc. capacity. From the first portion, silica, iron, aluminium, calcium, and magnesium were determined; from the second, sodium and potassium by a modification of the J. Lawrence Smith method; from the third, the sulphates; from the fourth, the phosphates; and, lastly, the manganese. No chromium was found. The results of the analyses were as follows:—

	Per cent of the ash.
SiO_2	0·78
Fe_2O_3	2·10
Al_2O_3	3·15
CaO	15·11
MgO	6·30
Na_2O	8·32
K_2O	40·26
SO_3	6·95
P_2O_5	14·87
Mn	0·94
Total	98·78

The remainder was organic matter that had escaped combustion and carbon dioxide. The ash was 4·1 per cent of the dried berry.

The Sugars.

For the sugar extraction about 100 grms. of the berries were placed in a litre flask, fitted to an upright condenser, and treated with successive portions of 95 per cent alcohol. The first extractions reacted acid to litmus-paper, and were of a deep reddish brown colour. At the end of 100 hours the colour had changed to amber, and a test with Fehling's solution showed only a small amount of sugar. Distilled water was then substituted for the alcohol, and eighty hours were required to extract the remainder of the sugars. This extraction was of a deep brown, almost black, colour. Both extractions were concentrated, and the percentage of sugar in each was determined as follows:—

One cc. of the alcoholic solution, diluted to 50 cc. with distilled water, was heated to boiling in a small beaker and titrated with Fehling's solution of such a strength that 10 cc. corresponded to 0·05 grm. of the sugar. To determine the end-point of the reaction, a drop of the solution was filtered through a folded filter-paper, and the clear filtrate tested for unreduced copper with a drop of a solution of glacial acetic acid and potassium ferrocyanide. A slight reddish tinge denoted the end of the reaction. The water extraction was determined in the same manner, using 25 cc. of undiluted extract. 17·17 grms. of sugar were found in the two extractions, which corresponds to 17·17 per cent of the dried berry.

Portions of the two extractions were mixed together and evaporated to dryness. The residue was almost black, had a bitter taste and an odour of scorched sorghum. This was purified by treating with alcohol and bone-black on the water-bath for several days. After filtering and evaporating, the residue was clear and of a light brown colour. With portions of 1 part of sugar, 2 parts of pure phenylhydrazine hydrochloride, 3 parts of crystallised sodium acetate, and 20 parts of water, the test pointed to fructose and dextrose. A heavy precipitate of osazones resulted in two to five minutes. This precipitate was filtered off, and attempts made to re-crystallise the osazones from alcohol, but no satisfactory results could be obtained.

The residue of the berries after the sugar extraction was dried and weighed. The loss in weight was about 69 per cent. The alcohol and water had also dissolved out acids, organic bases, proteids, colouring matter, &c.

The Oils.

The dried berries from the sugar extraction, weighing 31 grms., after being powdered somewhat with mortar and pestle, were placed in a 500 cc. flask and treated with successive additions of ether. One hundred hours was sufficient to remove all the oil. After removing the ether by distillation, the oil was thick and of a green colour. This colour, due to the presence of chlorophyll, was removed by heating several days with ether and bone-black, using an inverted condenser as before. The oil was then clear and colourless, but of such small volume that satisfactory tests could not be made with it.

At 0° C. the oil became white and almost hard. Its odour closely resembled that of castor oil. One saponification was made and the Koetstorfer number found to be 212·3. The oil was very easily saponified, a pleasant odour being given off during the operation. After the ether extraction the dried residue weighed 29·9 grms., a loss of 1·1 grm., or 1·1 per cent oil.

The Proteins.

A few of the berries were boiled in distilled water for a short time. Some of this solution was heated with nitric acid, giving a yellow colour which became an orange-red when made alkaline. This is a characteristic colour test for albumen. The nitrogen was determined by a modification of the Kjeldahl method, and found to be 0·59 per cent of the berries. This, computed as crude protein, gave a percentage of 3·68.

The Acids.

Portions of the sugar extraction were used for the acid tests. Tartaric and citric acids were found, with a trace of malic acid.

The Alkaloids.

Exhaustive tests were made for alkaloids, but no satisfactory results could be obtained. Dragendorf's methods were used.

Many thanks are due to Dr. Knight for his timely and valuable suggestions.

Cornell College, May 14, 1913.

Royal Institution.—A General Meeting of the Members of the Royal Institution was held on the 2nd inst., the Duke of Northumberland, President, in the Chair. Mr. L. R. Guthrie, Mr. G. W. Heath, and Mr. R. Malcolm were elected Members. The Chairman reported the death of the Right Hon. Lord Averbury, a Member of the Institution for 64 years, and a resolution of condolence was passed.

THE ANHYDROUS CONDITION AND STABILITY OF FUSED LITHIUM PERCHLORATE AND THEIR BEARING UPON THE ATOMIC WEIGHT OF SILVER.*

By THEODORE W. RICHARDS and MARSHALL W. COX,†
Harvard University, Cambridge, Mass.

IN a comprehensive research upon the atomic weights of lithium and silver, H. H. Willard and one of the present authors (Richards and Willard, Pub. Carnegie Inst. of Washington, No. 125) devised and perfected an entirely new method for determining the latter of the two atomic weights. This method involved the treatment of pure anhydrous lithium chloride with excess of perchloric acid, and the drying of the lithium perchlorate thus formed for a long time at a temperature of about 300°. From the weights of factor and product, together with the ratio of lithium chloride to silver (determined at the same time in another series of analyses made in the usual way), it is easy to calculate the atomic weight of silver with reference to that of oxygen in the following fashion, assuming that four times the atomic weight of oxygen is 64·000 :—

$$\frac{Ag}{64{\cdot}000} = \left(\frac{LiCl}{LiClO_4 - LiCl}\right)\frac{Ag}{LiCl}.$$

The value of the outcome depends entirely, as usual, upon the purity of the three solid substances concerned. Silver is capable of being made nowadays in a state of great purity. Lithium chloride also can be prepared in a state very free from contamination, even with water, by methods elaborated at Harvard ; but lithium perchlorate, which has been less studied, cannot be heated to a red heat without decomposition, and its freedom from volatile impurities is less certain. This fact was fully appreciated by the experimenters, and they promised to investigate further the question concerning the purity of the lithium perchlorate. Obviously any water retained by this salt would decrease the apparent atomic weight of silver, by increasing the denominator of the fraction within the parenthesis. On the other hand, any trace of decomposition suffered by the salt would have the opposite effect. The resulting contamination of the perchlorate by chloride or chlorate is easy to detect ; but the retention of minute traces of water is much more difficult to discover. The present investigation, which has been greatly prolonged because of the subtle nature of the problem, has primarily to do with the question as to the anhydrous condition of the lithium perchlorate, and we take pleasure in stating that the question, if not wholly settled, has now at least been carried much further than before. The evidence now available points towards the improbability of the retention of weighable amounts of water by lithium perchlorate at 300°. It is true that this result was not wholly unexpected, for the salt came to satisfactory constancy in weight, even at 280°, and a rise of 30° had no effect upon this weight. Moreover, one of us in collaboration with G. S. Forbes (Richards and Forbes, Carnegie Institution of Washington, Publication 69, 1907, p. 47), showed some time since that silver nitrate, a salt nearly as soluble as lithium perchlorate, retained practically no water at all at a much lower temperature, namely, 200°. Nevertheless, the outcome is satisfactory, and leads one to believe that the method under discussion for determining the atomic weight of silver is one of the very best.

The determination of the possible traces of water held by fused lithium perchlorate, which had been heated to constant weight at 300°, involved three main steps. In the first place, a series of experiments was carried out, in each of which about 12 grms. of the salt thus dried were heated to 400° for some time, while the quartz flask containing the fused salt was swept out with pure dry air. This air was afterwards passed through a heated tube containing silver wire and a weighed tube of phosphoric oxide ; the latter would catch and determine the water expelled. Even at this higher temperature the decomposition of the perchlorate was very slight. Then two further experiments were made with the temperature of the perchlorate raised to 430°, where the salt decomposed easily, and the evolution of the oxygen was continued until more than half of the salt was converted into lithium chloride. Finally, controlling experiments were carried out in which everything was maintained in precisely the same condition except that no perchlorate was present at all, and these blank trials served to evaluate the necessary errors of experimentation with the complicated apparatus. The crucial points of the whole problem were found to lie, first, in thoroughly sweeping out the whole apparatus with perfectly dry air for many hours before beginning the experiment, and, secondly, in filtering the pure air, both before it entered the flask containing the perchlorate and also before it entered the weighed drying tube. The filtration was necessary in the first case to remove the finest particles of dust which are only very inadequately held by the usual forms of purifying towers, and in the second case to hold the impalpable powder of lithium salt carried off by the bubbles of gas escaping from the fused mass. In each case the gas-filter consisted of a fine grained porous cup, suitably cemented within the glass apparatus, and the second gas-filter was heated during the experiment so that the lithium salt held there should not retain any of the water possibly expelled from the fused salt.

The outcome was as follows :—Three experiments, in which salt previously dried at 300° was further heated at 400°, showed gains in the pentoxide tube, amounting respectively to 0·00020, 0·00027, and 0·00029, in average 0·00025 grm. Two similar experiments, in which the temperature was raised to 430°, showed corresponding gains in the pentoxide tube, amounting respectively to 0·00026 and 0·00039, in average 0·00033. Finally, two "blank" experiments, in which no lithium perchlorate was present at all, showed gains amounting respectively to 0·00028 and 0·00034, in average 0·00031 grm.

In short, neither of the series in which lithium perchlorate was present deviated more from the control experiments than an account which might be due to the necessary errors of experiment. Clearly, lithium perchlorate previously dried at 300° cannot be made to evolve as much as one part in a hundred thousand of its weight of water by very drastic treatment.

At first sight this result seems to be conclusive ; one might be inclined, without further thought, to maintain that lithium perchlorate thus dried is truly anhydrous ; but the problem is not as simple as it appears. The fact that the salt *gives off* no water on decomposition does not necessarily prove that traces of water are not held as lithium hydroxide at the moment of decomposition ; for lithium hydroxide would not yield up its combined water by mere heating at a temperature even far above 430°. Nevertheless, a possible saving agency appears in this case in the material of the walls of the flask, which is greatly attacked as the salt decomposes. It is conceivable that any lithium hydroxide present would combine with the silica, and the water which might otherwise be held may thus be set free. For once the containing vessel, which so often introduces disturbing impurities, may actually aid the experimenter by its lack of resistance to the reagents which it holds.

Reassuring as this hypothesis may be, it has nevertheless not yet been proved, and one is not justified in considering the problem as wholly solved. A known amount of lithium hydroxide must be added to fused dry perchlorate, in order to discover if the mixture can be made to disengage its firmly imprisoned water by heating to 400° in contact with silica. This additional question will be tested experimentally in the near future. The mere heating of the perchlorate seems to have been carried as far in the

* Original communication, Eighth International Congresa of Applied Chemistry.

† The authors are much indebted to the Carnegie Institution of Washington for funds needed for the elaborate apparatus employed in this research.

present work as is worth while. The whole matter is a striking example of the subtlety and difficulty of a problem which might appear at first sight to be exceedingly simple.

The stability of lithium perchlorate evidently plays an important rôle in this performance. This stability was apparently affected in a very interesting way by the air-filter which removed the dust from the air passed over the salt. Without the dust-trap interposed in the air current, the salt bubbled in lively fashion at 350°; with it the temperature could be kept for an hour and a-half even at 400° without visible evolution of gas. The loss of weight in the latter case amounted to only a few hundredths of a per cent. Thus there seems to be some very finely divided matter in ordinary air—perhaps organic dust of almost sub-microscopic fineness—which catalyses the decomposition of lithium perchlorate by heat. This is an important fact in relation to the stability of the salt, as well as in its bearing on other similar cases.

In a few words the contents of this paper may be summarised as follows:—

Lithium perchlorate fused at 300° was found to lose no appreciable trace of water when gradually heated to 400° without much evolution of oxygen, or when quickly heated to 430° with far-reaching decomposition. Thus the salt used by Richards and Willard in their work on the atomic weight of lithium and silver appears to have been in this respect as pure as it could possibly be made. The present work therefore adds support to the value for silver 107·871, as found in the former work. Nevertheless, although as far as it goes the new work confirms the old, no one is yet in a position to state absolutely that a trace of water is not held by the residue left after the decomposition of the salt. This matter will be tested yet further in the future by methods already indicated; the question is of consequence, because it touches vitally one of the most important of all the atomic weights.

THE CALCULATION OF MINERAL FORMULÆ.

By WALDEMAR T. SCHALLER.

In the calculation of the ratios of a mineral analysis, it is customary to select arbitrarily one of the constituents as unity, or as some rational multiple of unity, and on this basis to calculate the ratios of the other constituents. As an example I will give the analysis of pearceite from the Veta Rica Mine, Sierra Majada, Coahuila, Mexico, as recently published by Frank R. Van Horn and C. W. Cook (*Am. Journ. Sci.*, 1911, [4], xxxi., 518).

	Analysis.	Ratios.		
S	17·46	0·5444	10·80	11
As	7·56	0·1008	2·00	2
Ag ..	59·22	0·2744 (*a*)	7·886	8
Cu ..	15·65	0·1231 (*a*)		
Sb	—			
	99·89			

(*a*) Considered as (Ag_2) and (Cu_2) respectively.

The ratios are sufficiently close to 11 : 2 : 8 to show that these are the correct numbers. In reality the ratios are very much closer to 11 : 2 : 8 than the figures given by Van Horn and Cook suggest, as will be shown below.

The first column from the ratios given above is reproduced below (1) with the molecular proportions for silver and copper combined, and all the quantities multiplied by 100 for convenience of calculation. When the lowest number is taken as unity it is readily seen that the ratios are approximately 5½ : 1 : 4. If the first figure be divided by two times 5½ (these numbers are doubled to avoid fractions), the second by 2×1, and the third by 2×4, the figures under (2) are obtained. These numbers should be nearly the same. Their average is 4·986. If now the ratios obtained from the analysis be divided by this average value, namely, 4·986, the figures given under (3) are obtained which are considerably closer to 11, 2, and 8 respectively than the ones given by Van Horn and Cook.

	1.		2.	3.
S	54·44	÷ (2×5½)	= 4·949	10·92
As	10·08	÷ (2×1)	= 5·040	2·02
Ag_2,Cu_2 ..	39·75	÷ (2×4)	= 4·969	7·97
Average			4·986	

Ratios such as those given above under (3) are still too far from the whole numbers they approximate for comparison as they stand. The figures should be reduced to multiples of approximate unity which can then be directly compared as follows:—

S	10·92	= 11×0·99 (3)	= 11×0·99
As	2·02	= 2×1·01	= 2×1·01
Ag_2,Cu_2 ..	7·97	= 8×0·99 (6)	= 8×1·00

These figures show that the ratios deducible from the pearceite analysis are, in fact, far closer to the whole numbers 11 : 2 : 8 than the ratios 10·80 : 2·00 : 7·886 given by Van Horn and Cook, which were obtained by arbitrarily selecting one of the numbers as unity. The form in which the last set of ratios is given above appears to express most accurately the relations derivable from the analysis. —*Journal of the Washington Academy of Sciences*, iii., No. 4.

THE DETERMINATION OF CHROMIUM AND VANADIUM IN STEEL.

By D. J. DEMOREST.

The writer recently described a method for the determination of vanadium in iron and steel, in which the vanadium alone is determined (*Journ. of Industrial and Engineering Chemistry*, iv., 249; CHEMICAL NEWS, cv., p. 244). Since chromium is present in many vanadium steels it is desirable to determine chromium along with the vanadium, and the present paper describes a modification of the above-mentioned method so as to easily determine the chromium and vanadium in the same sample. Nothing new is presented except that the details of the known method for chromium are worked out so that the author's method for vanadium can be combined with it.

The process is as follows:—2 grms. of the sample are dissolved in a 400 cc. flask by a mixture of 12 cc. strong sulphuric acid and 50 cc. of water. The flask is heated until solution is complete, when it is set off the hot plate and 25 cc. of nitric acid (sp. gr. 1·42) is very cautiously added. The iron is immediately oxidised to the ferric state with the evolution of much nitrous fumes. The solution is heated to boiling until the brown fumes are all driven off, then the flask is set off the hot plate and sodium bismuthate added until everything in solution is oxidised and the manganese appears as permanganic acid, which does not disappear on shaking. Now the solution is diluted to 200 cc., a little more sodium bismuthate added, and the solution boiled for twenty minutes to decompose the permanganic acid to manganese dioxide. It is then cooled by adding 50 cc. of water and filtered through asbestos. Then the volume is made up to 300 cc. and the solution cooled to tap-water temperature, when it is ready for the chromium titration after the addition of 5 cc. of syrupy phosphoric acid to decolorise the iron.

To titrate, run in N/100 ferrous sulphate solution until all chromium and vanadium are reduced. This can be told by testing a drop on a white plate with a drop of ferricyanide. If a blue colour is obtained, enough ferrous sulphate has been added. Then N/100 permanganate is added until a pink colour appears, which persists on shaking, and a few cc. more are added and the solution is

stirred for a minute. Then N/100 ferrous sulphate is added until the pink just disappears. The total ferrous sulphate minus the permanganate × 0·0001733 equals the chromium present.

Now to the solution enough ferrous sulphate to reduce the vanadium and a considerable excess is added, the solution mixed, and about 1 grm. of sized manganese dioxide is dropped in. The solution is shaken until a test with ferricyanide on a white plate shows that all ferrous iron has been oxidised. Then it is filtered through asbestos (using suction) and is ready for titration: N/100 permanganate is added until a persistent pink colour is obtained, then several cc. more are added and the solution is shaken for a minute. Now N/100 ferrous sulphate is added until the pink just disappears. The permanganate used minus the ferrous sulphate used × 0·00051 equals the vanadium present.

Notes on the Process.

The bismuthate oxidises the chromium, vanadium, and manganese to chromic acid, vanadic acid, and permanganic acid. Boiling destroys the permanganic acid and manganese dioxide precipitates and is filtered off. When ferrous sulphate is added, chromic and vanadic acids are reduced to trivalent chromium and quadrivalent vanadium; then when permanganate is added vanadium only is oxidised back, and the ferrous sulphate minus the permanganate measures the chromium.

Vanadium is again reduced by ferrous sulphate (not measured), the excess of ferrous sulphate oxidised by manganese dioxide, leaving the vanadium ready to be titrated.

The manganese dioxide must not be too fine. It should settle perfectly clear in a beaker of water in fifteen seconds. It must be natural or crystalline.

The following are some results obtained by the above method:—

Percentages vanadium.		Percentages chromium.	
Present.	Found.	Present.	Found.
0·145	0·143	0·078	0·086
0·145	0·145	0·155	0·160
0·145	0·147	0·155	0·157
0·145	0·145	0·233	0·236
		0·078	0·078
		0·233	0·225
0·145	0·147	3·100	3·095

A blank must be run on the chromium determination, as a little bit of MnO_2 persists in solution and runs uniformly the same.—*Journal of Industrial and Engineering Chemistry*, iv., No. 12.

THE MANUFACTURE OF SWEDISH FILTER PAPER.

By GUSTAF FORNSTEDT.

There are many different qualities of filter paper, depending upon the use for which they are intended, and they range from an ordinary filtering paper for household use to the fine double-extracted, ashless filter paper intended for very particular analytical work. As a rule, the ordinary qualities are machine-made, while, on the other hand, the finer qualities are hand-made.

Machine-made filter paper includes, among other varieties, beer filtering paper, a paper of about 180 lbs. weight, made chiefly from cotton rags, and used for filtering beer, as well as for the ordinary filtration of water. The paper is cut square and has 1¼-inch round holes perforated in each angle for the insertion of four metal bars on which the paper, alternating with perforated zinc plates, is threaded and screwed firmly together. Through these layers of paper and zinc the beer or other liquid is passed at a pressure of about 0·6 atmosphere; the dirt and impurities remain on the paper and the clean and clear liquid passes through.

Machine-made filter paper is used chiefly in the household and for technical purposes, while hand-made filter paper for scientific analyses is of better quality, though of different grades and make, according to the character of the analysis to be made. The paper being more or less quick filtering, it is made with regard to whether a mere purification of the liquid is intended or whether the substances collected on the paper are to be qualitatively or quantitatively determined.

Some qualities of filter paper, as white and grey woollen paper, are made generally in small paper mills which are not equipped with steam boilers. The rag is furnished "raw" in the beaters and beaten free, but care is taken to avoid lumps. The paper is made on a cylinder machine and taken wet on the hasp, from where it is cut by hand and hung up for drying. A rough mottled surface is produced by means of a coarse wire cylinder running on the wet paper web, the impression remaining very plainly after the paper is air dried.

The cleanest rag is, of course, used as material for filter paper, and it must be of the best quality and sorted with great care. It is important to pick out buttons and any pieces of metal that may be carried by the rags. In new cuttings from shirt and collar factories, used in the finest qualities, stray pins and needles give rise to much work and trouble. Iron is, of course, one of the worst impurities in a filtering paper.

The rag is boiled with sodium hydroxide (NaOH), because it gives a lower percentage of ash than lime, and for the same reason the old method of bleaching the half-stuff with chlorine is preferred to the use of chloride of lime in bleaching hollanders.

For chlorine bleaching a mixture of manganese, salt, and sulphuric acid is used in leaden retorts in about the following proportions:—

	Parts.
Binoxide of manganese	8
Sodium chloride	6
Sulphuric acid	5

Usually, however, a greater quantity of salt is used, because it contains a considerable amount of water.

After the rag is boiled, washed and beaten to halfstuff, it is dried in a centrifugal dryer and spread in layers on wooden poles in the bleaching chamber. This chamber is of concrete, lined with wood. After the bleaching chamber is filled with halfstuff the door is closed and chlorine admitted through an aperture in the roof. After all air has been withdrawn from the chamber it is well sealed, and the halfstuff, after absorbing the chlorine for several hours, is effectively bleached. Of late, in some mills this bleaching process has been considerably simplified. Liquefied chlorine pressed in steel bombs is used. The bomb is placed in hot water on a scale, a valve on top of the bomb, connected to the bleaching chamber with a rubber hose, is opened, and a certain amount of the liquefied chlorine makes its escape in the gaseous form, and is so forced into the bleaching chamber.

The analysis of boiled and bleached halfstuff shows the following ash percentages (silica and lime):—

New shirt cuttings, No. 1	0·039
Old linen, white	0·132
Old linen, grey	0·140
Coloured cottons	0·177
White cottons	0·107
Sulphite, bleached	0·298
Soda, bleached	0·4

It is, of course, a matter of great importance that the water used in the manufacture of filter paper should be as pure as possible, but it is impossible to avoid some ash-containing matter from being introduced to the halfstuff with the water of manufacture, and in the transportation

of the halfstuff and the process of drying. Generally the increase is from 0·02 to 0·05 per cent, depending on the state of the weather and the condition of the water.

The time consumed in beating varies according to the nature of the material. Halfstuff freshly bleached requires longer time than that which has been stored some time. Neither too free nor too slow stuff should be used for filter paper. Stuff that is too slow retards filtration—meaning the time taken for a given quantity of water of a certain temperature to filter through a paper of specific diameter. Paper made of too free stuff fails to keep back the finer grained sediments, such as sulphate of barium, &c.

Among the considerations to keep in mind in the manufacture of filter paper are the rate of filtration demanded, the ash content, resistance to sulphate of barium, fine holes, weight, and impurities.

To produce a filter paper of low ash percentage requires treatment with hydrochloric or hydrofluoric acid or a mixture of these acids, which will remove impurities like ferric oxide, alumina, lime, magnesia, and silica, and paper so treated is practically a pure cellulose paper. With hydrofluoric acid silica is removed, and with hydrochloric acid the other substances enumerated are dissolved away. After treatment with acids the paper should be thoroughly washed with distilled water, to remove the last traces of acidity.

To test the neutral reaction of the paper after washing, a solution of nitrate of silver is used to advantage. The wet paper is squeezed with the hand over a glass funnel and the water filtered into a test-tube. In another test-tube containing distilled water a few drops of test solution of nitrate of silver are added, and the same quantity is added to the water expressed from the washed filter paper. The two tubes are then compared against a black background. If not neutral, the water from the filter paper will show an opalescence due to the formation of insoluble chloride of silver from the chlorides remaining in the paper, and further washing is necessary. After this treatment the paper is pressed and hung out in open barns in order to freeze it.

By freezing the paper is made soft and porous, since the ice crystals formed in it serve to drive the fibres apart. Because of this the finest qualities of filter paper only can be made in the winter time in cold countries.

Experiments have been tried of subjecting paper that has been dried in a warm atmosphere to a subsequent freezing operation, in order to impart the desired softness and porosity, but it has been found that paper treated in this way does not become soft, and it never comes up to the standard of the best Swedish filter paper.

Extracted filter paper is practically ashless, the ashes amounting to about 0·015 per cent of the weight of paper, and is often negligible, not being taken into account in quantitative analytical work.

The most careful, accurate work is necessary in any determination of the ash content of a paper. The instruments required consist of a spacious drying apparatus of copper, two exsiccators, one large and one small, a platinum crucible (about 0·7 oz.) with cover, a stand, a spirit lamp, a blast lamp or Bunsen burner, and a particularly exact balance scale.

The larger exsiccator is used for the dry paper and the smaller for the platinum crucible. Every time the crucible is used it must be cleansed with the finest sand, which has been previously boiled in diluted hydrochloric acid, dried, fired, and kept in the exsiccator until the next time it is used. The scale placed on a table fixed to the wall ought to be of superior construction for fine analytical determinations. Soot must naturally be guarded against in the incinerating operation, as the particles would lead to error in the weighing and conduce to an early deterioration of the crucible.

The manipulations are as follows:—The sample is first dried in the drying apparatus at a heat of 190° to 210° F. It is then transferred to the exsiccator for fifteen minutes, and afterwards cut in small pieces and put in the cleaned and weighed crucible. The crucible is supported on its stand and the cover adjusted so that air may enter. The crucible is first heated red hot, at which point the hydrocarbon volatilises; the heat is then increased for twenty minutes, until the crucible glows white hot. After the ash turns white or grey-white the crucible is placed in the exsiccator for ten minutes and weighed; the incineration is then continued until a constant weight is obtained.

If the crucible weighs *a* grm., the crucible and paper *b* grm., and crucible and ash *c* grm., the following formula is obtained.

Paper and crucible	= *b* grm.
Crucible	= *a* grm.
Paper	= $(b-a)$ grm.

Hand Brace.

a grm.

Ash and crucible	= *c* grm.
Crucible	= *a* grm.
Ash	= $(c-a)$ grm.

Hand Brace.

b grm.

The following figures giving the analysis of ash from fine filter paper are of interest.

I. *Prof. V. Wich.*		II. *Prof. Brunner.*	
SiO_2	31·876	SiO_2	30·63
Al_2O_3	14·364	AlO_3	14·86
Fe_2O_3	9·357	$Fe_2O_3 + P_2O_5$ ..	5·08
P_2O_5	0·238	MnO	1·74
$MnO \cdot Mn_2O_3$ ..	7·637	MgO	7·84
MgO	11·301	CaO	26·28
CaO	21·381	Alkali	13·57
Alkali	2·162		100·000
SO_3	1·684		
	100·000		

The best filter paper is made in Grycksbo, Sweden. In the work of manufacture through a long period of years a practical and effective method of extraction has been employed. Being the most northerly hand-paper mill in the world, there is a long, splendid winter which is favourable for freezing the paper. The water is clear as crystal and practically chemically pure, having its origin in the Delecaalian mountains. Berzelius, the world renowned chemist, esteemed the Swedish filter paper to be the best in the world, and the mill still maintains its reputation, the paper being in demand over all the old and new world, while the United States takes the bulk of it.

The paper is stamped out in different sizes from 5·5 centimetres to 18·5 centimetres, and is packed in birch bark boxes, which are lined with thin sheets of zinc, hermetically sealed for export to foreign countries.

A good standard of the efficiency of a paper as a filtering medium is represented by the following factors: with a paper having a diameter of six inches, the maximum time for filtration of six cubic inches of water at 90° F. should be 140 seconds, the minimum time 90 seconds.—*Chemical Engineer*, xvii., No. 1 (from *Paper*).

Catalytic Hydrogenation of Acetone.—A. Lassieur.—The hydrogenation of acetone by the method of Sabatier and Senderens at temperatures above 200° gives neither isopropyl alcohol nor pinacone, but large quantities of methylisobutyl ketone, smaller quantities of valerone, and also more condensed products. Probably the acetone first condenses with itself with elimination of water, giving mesityl oxide and isophorone, which are finally hydrogenated.—*Comptes Rendus*, clvi., No. 10.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, May 22nd, 1913.

Sir ARCHIBALD GEIKIE, K.C.B., President, in the Chair.

THE Bakerian Lecture was delivered by Prof. Sir J. J. THOMSON, O.M., F.R.S., on "*Positive Rays of Electricity.*"

The first part of the paper contains a discussion of the evidence afforded by the positive rays as to the nature of the ionisation of the gases in a discharge tube and the properties of atoms. The positive rays consist of :—

1. Atoms with one positive charge.
2. Molecules with one positive charge.
3. Multiple charged atoms.
4. Atoms with one negative charge.
5. Molecules with one negative charge.

All the diatomic gaseous elements which have been examined furnish both atoms and molecules with single charges. The proportion of atoms to molecules varies very largely with the conditions of the electric discharge, and evidence is given that the charged atoms and molecules are produced by different processes. It is suggested that the ionisation which gives rise to molecules is due to cathode rays, while the charged atoms are produced by the impact of charged atoms and molecules.

All the elements examined, with the significant exceptions of hydrogen and a substance of atomic weight $3(X_3)$, furnish, under certain conditions, atoms with more than one charge. The power of acquiring multiple charges seems to be connected with the atomic weight rather than with the valency or other chemical property of the atom. Thus the atom of mercury, the heaviest atom investigated, can have as many as 8 charges, crypton 5, argon 3, while the lighter atoms, as a rule, have only 2. No undoubted case of a doubly-charged *molecule* of an element or compound has yet been discovered.

The negative charge is found on the atoms of some elements, *e.g.*, hydrogen, oxygen, carbon, sulphur, chlorine, but not on the atoms of nitrogen, helium, neon, argon, or mercury. It may be regarded as an indication of the chemical activity of the atom, in so far as this depends upon the intensity of the electric field outside the atom. No negatively electrified molecules of compounds have been observed; the only cases of negatively electrified molecules of elements are those of oxygen and carbon, and these only occur when the elements are liberated from special types of compounds.

The second part of the paper deals with the use of these rays as a method of chemical analysis. Several applications of the method are considered. The first of these is to the detection of rare gases in the atmosphere. It is shown that while none of the heavier gases in the atmosphere occurring in quantities comparable with that of Xenon have escaped detection, this is not the case with the lighter gases.

"Neon," it is shown, is not a simple gas but a mixture of two gases, containing a large quantity of a gas of atomic weight about 20, and a much smaller quantity of one with an atomic weight about 22. The "22" gas was first observed in samples of residues of liquid air supplied by Sir James Dewar, and has since been found in every specimen of neon examined, including a specimen kindly supplied by M. Claud, of Paris, and a very carefully purified sample of neon prepared by Mr. Watson. The sample from M. Claud contained a small quantity of a substance with atomic weight 3 whose properties are discussed later on.

Another application of this method was to the analysis of the gas in a small glass tube in which 30 mgrms. of radium bromide had been sealed for more than ten years; in addition to helium, the gas contained consider ble quantities of "neon" or some element with very nearly the same atomic weight; there was also a trace of argon in the gas, a little more than I should have expected from the volume of air in the tube, although the difference was not very great.

The other application of the method is to the investigation of the properties of a substance for which $m/e = 3, X_3$. This gas is given off by most solids when they are bombarded by cathode rays. Reasons are given for concluding that the substance is not the carbon alone with four charges.

The gas has the following properties :—

It can pass through tubes containing red-hot copper oxide, and then over potash without being absorbed.

It is not changed when sparked for a long time with an excess of oxygen, the oxygen being subsequently removed by phosphorus.

It can pass over metallic sodium without being absorbed, nor does it disappear when heated along with sodium vapour.

It is absorbed by charcoal cooled with liquid air, but it can circulate through a glass spiral immersed in liquid air without being condensed.

It combines with mercury vapour when an electric discharge is sent through the mixture; it also combines to some extent with red-hot copper when passed slowly over it. If stored over mercury vapour it seems to diminish, though very slowly. I have detected it after it has been stored for several weeks.

The study of the positive-ray photograph indicates that the substance is monatomic, and generally it seems to be similar in its behaviour to the inert gases, although its chemical properties are apparently a little more energetic.

CHEMICAL SOCIETY.

Ordinary Meeting, May 15th, 1913.

Prof. W. H. PERKIN, LL.D., F.R.S., President, in the Chair.

REFERENCE was made to the death, on April 29th, 1913, of Mr. Matthew Algernon Adams, of Maidstone, who was elected a Fellow on February 15th, 1877.

The PRESIDENT announced that the Council have proposed the following gentlemen as Honorary and Foreign Members, and that a ballot for their election will be held at the next Ordinary Scientific Meeting on Thursday, June 5th: Prof. Dmitri Petrovitsch Konovaloff (St. Petersburg); Prof. Alfred Werner (Zurich).

The PRESIDENT also read the following statement which the Council have received with reference to the Van't Hoff Memorial Fund :—

Report of the Van't Hoff Committee, April 18th, 1913.

The united Committees of Amsterdam and Rotterdam have received up to the present a sum of Fl.56,000, about Fl.6,000 having been contributed by foreign countries. A sum of Fl.35,000 has been set aside to defray the cost of the statue to be erected in Van't Hoff's native town, Rotterdam, after the design of Mr. Charles van Wijk, of The Hague. It is hoped that the inauguration may take place during the course of 1915. After the expenses have been deducted, the remainder will be allotted to the Van't Hoff Memorial Fund for the advancement of original research in pure and applied chemistry. Probably the Royal Academy of Science of Amsterdam will undertake to manage the capital and to assign the annual grants.

Certificates were read for the first time in favour of Messrs. William Rhys-Davies, Swan Arcade, Bradford; Roy Gonçalves Glenday, B.A., Emmanuel College, Cambridge; Victor Lefebure, B.Sc., 25, Belitha Villas, Barnsbury, N.; Duncan James Macnaughten, 31, Clonmel Road, Fulham, S.W.; Percy Cyril Lesley Thorne, B.A., Borough Road Training College, Isleworth; Jeremiah Twomey,

B.Sc., 21, Onslow Road, Elm Park, Liverpool; Thomas Howard Young, 118, Scotia Street, Winnipeg, Canada.

Messrs. A. J. Ewins and H. Finnemore were elected Scrutators, and a ballot for the election of Fellows was held. The following were subsequently declared as duly elected:—John Percy Batey, M.Sc.Tech.; Horace George Battye; George Frederick William Blackburn; Edward Cahen; Alexander Caruth; Noël Guilbert Stevenson Coppin, M.Sc.; Arthur Ernest Crutchley; Vasanji Premji Dalal, M.A., B.Sc.; Harold Davies; Alfred Gilbert Dix, B.Sc.; Herbert Garland; Fritz Haber; Percy Wolmer Hill; Harold Edward Pollock Hodsoll; Thomas Arthur Holroyd, B.Sc.; Percy Hutchinson, B.Sc.; Hilton Ira Jones; Darab Dinsha Kanga, M.A.; Douglas Rayment Keller, B.Sc.; Emmanuel Francis Kur; Joseph Stuart Lawson; Harold Charles Lloyd, B.Sc.; John Francis McCann; Harry Bertram Maynard; Bhaichand Anupchand Mehta, M.A.; Arthur George Abraham Miller, B.Sc.; Ferrand Paget; Francis Martin Potter, B.Sc.; Julien Pierre Frederic Pougnet; Kali Prosonuo Rai, M.A.; Arthur Samuel Robinson, B.Sc.; John Robert Ruffley; Reginald William Rusby; Hormusji Kharschedji Sahiar, M.A.; Sosale Garalpury Sastry, B.A.; Herbert Sutcliffe Shrewsbury; William James Stansfield; Thomas Watson; Cornelius Williams, B.Sc.; Thomas Harrison Winstanley; Clifton Wyver; William John Young, D.Sc., M.Sc.

Of the following papers, those marked * were read:—

*140. "*Studies of Dynamic Isomerism.* Part XV. *The Influence of Light on Isomeric Change.*" By THOMAS MARTIN LOWRY and HAROLD REUBEN COURTMAN.

Several substances which readily undergo isomeric change on dissolution were exposed to the action of ultra-violet light by enclosing the solutions in a silica polarimeter tube surrounded by a silica waterjacket and placed in close proximity to a silica mercury lamp. Of nine substances examined, only two showed any marked acceleration of isomeric change. In the case of aminomethylenecamphor the increase of velocity was confined to the period of exposure to light, but in the case of benzoylcamphor it persisted after the light was extinguished, as if some chemical catalyst had been produced in the solution.

*141. "*Derivatives of o Xylene.* Part III. *The Presence of a Mobile Nitro-group in each of the Two Trinitro-o-xylenes.*" By ARTHUR WILLIAM CROSSLEY and WALTER RYLEY PRATT.

3 : 4 : 5-Trinitro- and 3 : 4 : 6 trinitro *o*-xylenes each contains a mobile nitro-group occupying position 4 in the former and position 3 in the latter compound. The groups are replaced by the amino-group when treated with alcoholic ammonia (*Trans.*, 1911, xcix., 2345), and it has now been found that many substituted amines behave similarly to ammonia. Derivatives have been prepared from the following primary amines:—Methylamine, ethylamine, aniline, *p*-toluidine, *o*- and *p*-anisidine, benzylamine, and, using the secondary amines, dimethylamine and piperidine. Ortho- and metanitroaniline and methyl-aniline appear to have no action on the trinitroxylenes, and although interaction takes place between both trinitroxylenes and diethylamine, also *p*-phenylenediamine, only resinous products and no crystalline derivatives could be obtained.

It is interesting to note that the mobile group in 3 : 4 : 5-trinitro-*o*-xylene is situated ortho- to the two other nitro-groups, whereas in 3 : 4 : 6-trinitro-*o*-xylene it is ortho- to one and para- to the other, both positions which, as already noticed, seem especially favourable to replacement.

DISCUSSION.

Dr. FLÜRSCHEIM confirmed Prof. Crossley's conclusion that the mobility of a nitro-group in 3 : 4 : 5-trinitro-*o*-xylene should even be exceeded in tetranitroaniline. He agreed with the President's view that this fact could not be entirely accounted for by the influence of the additional nitro-group in the para-position to the mobile group, since the effect of a para-nitro-group would be small in comparison with that exercised by the two nitro-groups already present in the ortho-positions. The methyl groups in trinitro-*o*-xylene would, however, largely account for the difference. Methyl was known to lower the reactivity of chlorine in chlorodinitrobenzene and that of a nitro-group in trinitrobenzene; also the tendency of *m*-dinitrobenzene and *s*-trinitrobenzene to form additive compounds with amines, the dissociation constant of nitrobenzoic acids, &c. (compare also Blanksma, *Rec. trav. chim.*, 1906, xxv., 175).

Prof. Crossley's proof that 3 : 4 : 6-trinitro-*o*-xylene and Meldola's trinitroacetylaminophenol exchanged their nitro-groups in different positions appeared to be of considerable interest. The cause might possibly be traced to the effect which the residual affinity of the hydroxyl group in Meldola's compound must have on the amount of affinity at the disposal of the various benzenoid carbon atoms for binding the nitro-groups.

Dr. R. SELIGMAN asked whether Prof. Crossley had noticed any difference in the mobility of the nitro-groups in 3 : 4 : 5-trinitro- and 3 : 4 : 6-trinitro-*o*-xylenes. In view of the form which the discussion had taken, several speakers having ascribed the mobility to the ortho-position of two nitro-groups rather than to their para-position, it seemed that any such observation by Prof. Crossley should settle the question, as he had two compounds differing only in the relative positions of the nitro-groups.

In reply, Prof. CROSSLEY stated that at the present time no measurements of value had been made of the relative mobility of the nitro-groups in 3 : 4 : 5-trinitro- and 3 : 4 : 6-trinitro *o*-xylenes. Many experimental difficulties would have to be overcome before this would be possible, and work with this object in view was now being undertaken.

*142. "*Derivatives of o-Xylene.* Part IV. *Synthesis of* 4 : 5-*Dibromo*-3-*o*-*xylenol.*" By ARTHUR WILLIAM CROSSLEY and SYDNEY SMITH.

4 : 5-*Dibromo* 3-*o*-*xylenol*, prepared by the method already indicated (*Proc.*, 1912, xxviii., 333), crystallises from aqueous alcohol in glistening flattened needles, melting at 97°. The *acetyl* derivative separates from light petroleum in large hexagonal prisms, melting at 78°, and the *benzoyl* derivative crystallises from alcohol in small transparent rhombs, melting at 153°.

*143. "*Synthetical Preparation of the* d-*Glucosides of Sitosterol, Cholesterol, and some Fatty Alcohols.*" By ARTHUR HENRY SALWAY.

It has already been shown (*Trans.*, 1913, ciii., 399) that ipuranol and some allied compounds occurring in plants, to which specific names had been assigned, are phytosterol glucosides. In many cases these compounds appear to consist of sitosterol-*d*-glucoside, $C_{27}H_{45}O\cdot C_6H_{11}O_5$, whilst in other instances they seem to be a mixture of the latter with the glucoside of stigmasterol, $C_{30}H_{49}O\cdot C_6H_{11}O_5$.

The author gave a description of the synthetic preparation and properties of some glucosides of the above-mentioned type, and also of the glucosides of some fatty alcohols. The compounds which have now been prepared and characterised are as follows:—(1) *Sitosterol* d-*glucoside*, $C_{27}H_{45}O\cdot C_6H_{11}O_5$ (m. p. 295—300°); (2) *cholesterol*-d-*glucoside*, $C_{27}H_{45}O\cdot C_6H_{11}O_5$ (m. p. 285); (3) *Myricyl*-d-*glucoside*, $C_{30}H_{61}O\cdot C_6H_{11}O_5$ (m. p. 99°); (4) *ceryl*-d-*glucoside*, $C_{27}H_{55}O\cdot C_6H_{11}O_5$. This compound was obtained in two modifications, melting at 94° and 135° respectively; and (5) cetyl-*d*-glucoside, $C_{16}H_{33}O\cdot C_6H_{11}O_5$. Although this glucoside was first synthetically prepared by Fischer and Helferich (*Annalen*, 1911, cccl xxxiii., 68), it has now been somewhat more completely characterised.

Several derivatives of the above-mentioned glucosides have likewise been prepared.

DISCUSSION.

In reply to Dr. Forster, Dr. SALWAY stated that the substances previously designated as ipuranol, trifolianol, cluytianol, &c., were so named in order to indicate their origin and alcoholic nature, and no other method of pro-

cedure was possible in the case of new organic compounds of unknown constitution. Since it had now been ascertained that the group of substances referred to were phytosterol glucosides, it was possible to designate them collectively as *phytosterolins*.

*144. "*The Rotatory Dispersive Power of Organic Compounds.* Part I. *The Measurement of Rotatory Dispersion.*" By THOMAS MARTIN LOWRY.

A description was given of methods and apparatus suitable for ordinary laboratory use in the measurement of rotatory dispersion. Special importance is attached to measurements of rotatory power for the mercury lines of wave-length 5461 and 4359.

*145, "*The Rotatory Dispersive Power of Organic Compounds.* Part II. *The Form of the Rotatory-Dispersion Curves.*" By THOMAS MARTIN LOWRY and THOMAS WILLIAM DICKSON.

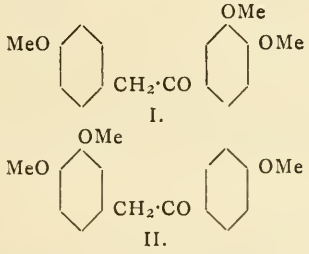
It was shown that the rotatory dispersion in a large number of simple organic compounds can be expressed by the formula—

$$\alpha = \frac{\alpha_0}{\lambda^2 - \lambda_0^2},$$

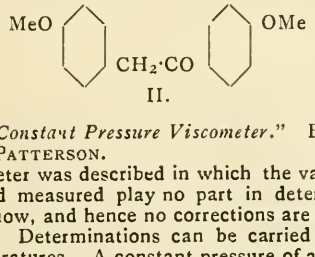
where α_0 is the "absolute rotatory power" and λ_0^2 is the "dispersion constant" of the substance.

146. *Synthesis of Unsymmetrical Derivatives of Deoxybenzoin.*" By JOHN CANNELL CAIN, JOHN LIONEL SIMONSEN, and CLARENCE SMITH.

The authors have prepared *β-keto-α-4-methoxyphenyl-β* 3 : 4-*dimethoxyphenylethane* (I.) by condensing p-*methoxyphenylacetyl chloride* with veratrole, and *β-keto-β-4-methoxyphenyl-α-3* : 4-*dimethoxyphenylethane* (II.) by condensing 3 : 4-dimethoxyphenylacetyl chloride with anisole. *Oximes* of both compounds were also prepared.



I.



II.

147. "*A Constant Pressure Viscometer.*" By WILLIAM HAMILTON PATTERSON.

A viscometer was described in which the varying levels of the liquid measured play no part in determining the pressure of flow, and hence no corrections are required for density, &c. Determinations can be carried out at different temperatures. A constant pressure of air drives the liquid slowly through a narrow-bore tube, which is made of fused silica.

148. "*The Chemical Nature of some Radioactive Disintegration Products.*" Part II. By ALEXANDER FLECK.

In accordance with the theoretical conclusions advanced independently by K. Fajans and F. Soddy since the first part of this paper was published (*Trans.*, 1913, ciii., 381), it has been found that radium-A is chemically non-separable from radium-F (polonium), and that thorium-D and actinium-D are, in the same way, similar to thallium. The non-separability of radium-A from polonium was proved by placing two plates of different metals simultaneously in a solution containing radium-A, -B, -C, and -F for one minute. There were thus different potential differences forcing the ions of the radio elements on to the plates, but it was found that the same relative quantities of polonium and radium-A were deposited on each of the various pairs of metals tried.

The case of the similarity of the -D members and thallium was shown by a number of reactions and by fractionally precipitating thallium first as chloride and finally as sulphide from an alkaline solution. The concentration of the active substance was not altered in any of the fractions.

Actinium B was also proved to be non-separable from lead by a series of fractional precipitations of lead sulphate, in which it was shown that the concentration of actinium B is constant in all tractions.

149. "*The Estimation of Small Quantities of Lead.*" By ALFRED VINCENT ELSDEN and JOHN FIRTH STANSFIELD.

Wilkie's observations (*Journ. Soc. Chem. Ind.*, 1909, xxviii., 636) on the co-precipitation of lead and ferric iron by ammonia have been confirmed, and this property has been applied to the separation and estimation of small quantities of lead. A new method for the estimation of lead in the presence of iron was described, and examples were given.

150. "*The Iodocinnamic Acids.*" By THOMAS CAMPBELL JAMES.

Three monoiodocinnamic acids are at present recorded in the literature, all of which are classed as *β*-iodocinnamic acids. The author has prepared a fourth isomeride by treating *αβ*-dihydroxy-*β*-phenylpropionic acid (Fittig and Ruer, *Ann.*, 1892, cclxviii., 27) with a concentrated solution of hydriodic acid at the ordinary temperature.

An examination of the properties of the isomerides indicates that Michael's *β*-iodocinnamic acids (*Ber.*, 1901, xxxiv., 3658) are correctly described, whilst that prepared by Ortoleva (*Gazetta*, 1899, xxix., [1], 504) is *α*-iodocinnamic acid, and the new isomeride is *α-iodoallocinnamic acid*.

151. "*Rate of Evolution of Gases from Supersaturated Solutions.* Part I. *Influence of Colloids and of Suspensions of Charcoal on the Evolution of Carbon Dioxide.*" By ALEXANDER FINDLAY and GEORGE KING.

The velocity of escape of carbon dioxide from supersaturated solution in water, in solutions of potassium chloride, in colloidal solutions of gelatin, starch, dextrin, ferric hydroxide, peptone, agar, and in aqueous suspensions of platinum and charcoal, has been studied. Measurements were made of the velocity of spontaneous evolution of gas from unagitated solutions, but attention was devoted mainly to the study of evolution from well-agitated solutions, a suitable apparatus and method of working having been devised, whereby the very rapid evolution of gas can be accurately measured. Whereas, in the case of pure water and solutions of potassium chloride, the velocity of evolution is very nearly proportional to the degree of supersaturation, this no longer holds good in the case of colloidal solutions, which also show marked differences among themselves. In carrying out the measurements, the solutions were first saturated with carbon dioxide under a pressure of about 760 mm. above atmospheric; the pressure was then reduced to that of the atmosphere, and the gas evolved was measured. On reducing the pressure, a period of quiescence, during which practically no gas was evolved, occurred in the case of most of the solutions, but in the case of ferric hydroxide and of peptone no such quiescent period was obtained, and spontaneous evolution of gas took place immediately the pressure was reduced.

152. "*Viscosity Maxima and their Interpretation.*" By FERDINAND BERNARD THOLE, ALBERT GEORGE MUSSELL, and ALBERT ERNEST DUNSTAN.

In view of the investigations recently published by Denison and by Kurnakov and Schemtschushni on the interpretation of maxima in the viscosity composition curves of liquid mixtures, the authors have investigated more fully the various types of curves obtained for different liquids, particularly with those pairs of compounds the freezing-point composition curves of which have been determined.

The results show that in general liquids which give a mixture of maximum melting-point give also a mixture with

a maximum viscosity, although in certain cases a sagged curve may be obtained if one of the components has a higher molecular complexity than the compound formed.

The position of the point of maximum viscosity is not dependent entirely on the composition of the complex, although in cases where the two components have a strong mutual chemical affinity the maximum viscosity is found with the mixture of simple molecular composition; for example, thiocarbimides-amines and sulphuric acid water.

153. "*Condensation of Aromatic Aldehydes with Pyruvic Acid.*" By Eva Lubrzynska and Ida Smedley.

Piperonal, anisaldehyde, and cinnamaldehyde were condensed with pyruvic acid in very dilute alkaline solution; the $\beta\gamma$ unsaturated α-ketonic acids formed were oxidised with hydrogen peroxide in neutral solution, and the corresponding $\alpha\beta$-unsaturated acids isolated.

154. "*Isolation and Purification of Cerebrone.*" By Arthur Lapworth.

During the last three years the author has frequently had occasion to prepare pure cerebrone from large quantities of brain. He has found it most satisfactory to extract the material, partly dried in spirit, with boiling methyl alcohol, to precipitate most of the phosphatic materials by neutralising the hot liquid with methyl-alcoholic baryta, subsequently decanting the clear, supernatant liquid, and destroying the remaining phosphatides by adding excess of powdered barium oxide and boiling for several hours. The solvent is then mostly removed, and the residue rendered slightly acid with glacial acetic acid in the presence of chloroform, which is subsequently removed by distillation, and the cerebrone, mixed with cholesterol, extracted by methyl alcohol. Complete separation of phosphatides and cholesterol from the cerebrone may be effected in several ways, of which continuous extraction with boiling acetone is the most efficient (compare Lorrain Smith and Mair, *Journ. Path. Bact.*, 1910, xv., 122; 1911, xvi., 131; Lapworth, *Ibid.*, 1911, xvi., 255; Loening and Thierfelder, *Zeit. Phys. Chem.*, 1912, lxxvii., 202).

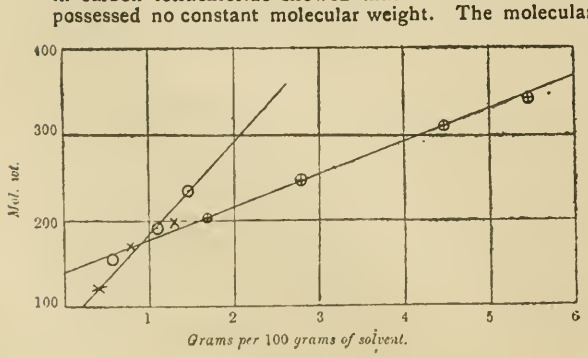
155. "*Cyaphenine.*" By John Edwin Mackenzie.

The formula generally assigned to cyaphenine is $(C_6H_5{\cdot}CN)_3$, but its molecular weight does not appear hitherto to have been determined directly.

In some experiments performed with the object of obtaining benziminohydrin from benzimino-ethyl ether hydrochloride according to the equation:—

$$C_6H_5{\cdot}C\overset{NH,HCl}{\underset{OEt}{=}} + AgOH = = C_6H_5{\cdot}C\overset{NH}{\underset{OH}{=}} + AgCl + EtOH,$$

cyaphenine was found among the products of the reaction. A number of determinations of the elevation of the boiling-point of solutions of cyaphenine [prepared by Eitner and Krafft's method—*Ber.*, 1892, xxv., 2266; it was further purified by distillation under diminished pressure; the product melted at 233° (corr.)] in benzene and in carbon tetrachloride showed that in these solutions it possessed no constant molecular weight. The molecular weights obtained in solutions of the concentration stated are plotted on the diagram.



The cryoscopic method was found unsuitable on account of the very small solubility of cyaphenine in the solvents available. The vapour density was then determined, and gave results agreeing with those required for the formula $(C_6H_5{\cdot}CN)_3$.

*Molecular-weight Determinations of Cyaphenine by the Ebullioscopic Method.**

$C_{21}H_{15}N_3$ requires M.W. = 309.

Benzene (+) *Series* (Solvent: 9·8561).

w.	Δ°	M.W.
0·1451	0·195	203·8
0·2749	0·305	246·8
0·4399	0·390	309·0
0·5377	0·430	342·6

Carbon Tetrachloride (·) *Series* (Solvent: 20·377 grms.).

0·1156	0·1754	155·3
0·2221	0·2729	191·7
0·2963	0·2975	234·6

Carbon Tetrachloride × *Series.*

0·0936	0·1688	119·9
0·1746	0·2239	168·6
0·2872	0·3120	199·1

These results have been plotted in the diagram above, and as will be seen, the molecular weight increases steadily with increase of concentration of the solution.

The vapour density was determined by V. Meyer's displacement method, the vaporisation taking place at the boiling-point of sulphur:—

w.	V. moist air (cc.).	*t.*	P (mm.).	M.W.
0·1816	14·0	18°	753	319·0
0·1928	14·7	17°	753	320·5

$C_{21}H_{15}N_3$ requires M.W. = 309.

It may therefore be concluded that cyaphenine at a temperature of about 450° has the above formula, but that in chloroform and benzene solutions it undergoes dissociation and association.

156. "*Note on the Identification of Proline.*" By Wilhelm Gluud.

Racemic proline is usually identified by its characteristic copper salt, which crystallises from aqueous solution with two molecules of water. In a recent paper Emil Fischer and Gerlach (*Ber.*, 1912, xlv., 2453) showed that the copper salt of pyrrolinecarboxylic acid may be confused with the copper salt of proline, and that a complete analysis is necessary to distinguish between the two.

In the case of allylglycine, which has the same empirical formula as proline, such a method would be of no value. It was therefore desirable to prepare and examine the copper salt of allylglycine, in case it could be mistaken for that of proline.

N-Allylglycine (compare Alpern and Weizmann, *Trans.*, 1911, xcix., 84) was prepared from chloroacetamide and allylamine as follows:—8 c.c. of allylamine were mixed with 4 grms. of chloroacetamide, and the mixture cooled in ice until the reaction had moderated. The liquid was left overnight at room temperature, then diluted with 200 c.c. of water, and 30 grms. of recrystallised baryta were added. This mixture was heated on a water-bath for three-quarters of an hour, then boiled for fifteen minutes, and evaporated to dryness in a vacuum. The residue was dissolved in 500 c.c. of water, and the baryta precipitated with carbon dioxide. The filtrate was poured into 20 c.c. of 5N-sulphuric acid, and 80 grms. of lead oxide (previously purified by boiling with water) were added. The

* The constants for benzene and carbon tetrachloride employed in the calculations were 27 and 48 respectively.

whole mixture was boiled for twenty minutes, then rapidly filtered, and the lead precipitated with hydrogen sulphide. The solution was heated to boiling, then filtered, and the filtrate boiled with precipitated copper oxide for half an hour, rapidly filtered, and the dark blue filtrate concentrated in a vacuum.

The *copper* salt separates in blue crystals shot with violet, in the form of squares or hexagonal plates (2·3 grms.), which can be readily recrystallised from water—

0·1165 gave 0·0320 CuO. Cu = 21·95.

0·2093 gave 16·8 c.c. N_2 at 16° and 768 m.m. N = 9·48.

$C_{10}H_{16}O_4N_2Cu$ requires Cu = 21·79; N = 9·61 per cent.

When dried at 100°/10—12 mm., over phosphoric acid, there is no change in weight or colour of the salt. The copper salt thus prepared is very similar in appearance to that of proline, but it contains no water of crystallisation, so that estimation of water and copper in a supposed copper salt of proline is sufficient to exclude the presence of allylglycine.

On heating the copper salt of allyglycine, the same odour is noticed as on heating that of proline, but further experiments are necessary to identify the decomposition products.

NOTICES OF BOOKS.

Laboratory Text-book of Chemistry. By V. Seymour Bryant, M.A. Part I. London: J. and A. Churchill. 1913.

This book contains a course of practical work in elementary chemistry suitable for boys about fourteen years of age who are beginning the subject. In some respects the course resembles that usually followed in teaching chemistry many years ago, the early lessons being on elements, compounds, and mixtures, the atomic theory, and chemical equations. But the practical work is generally intended to be performed by the student himself, and the subject is developed more logically than it used to be. The treatment is historical, and the details of many classical experiments are described. The experimental directions are sufficiently full for the students to need comparatively little help or supervision in the great majority of cases. The arrangement of the book is convenient and should commend itself to teachers. After the descriptions of the experiments, blank spaces are left for the student's own observations and for any numerical data obtained, and blank pages are also left for the answers to the sets of questions included in every chapter and for descriptions of the extra practical work which is suggested for the benefit of the quicker boys.

One Hundred Simple Exact Mathematical Proofs that the Valencies of Carbon are Unequal. By Hawksworth Collins. London: Morton and Burt, Ltd. 1913.

In this book the author gives diagrams showing the methods by which the specific gravity of chemical compounds can be calculated. He assumes that the atomic volume of carbon is 0·71, while that of hydrogen varies according to the position of the atom in the molecule, but is always very much greater. Thus, in one position it is 9·95, and in another 5·76. Chlorine has the same volume in every position, viz., 23·01, while bromine has the same in two positions, and iodine in three. The specific gravities of 100 organic compounds of varying degrees of complexity have been calculated, and the results obtained certainly merit attention, for in all cases they are remarkably close to the observed values. The author claims that the results have been reached by discovery and not by guesswork, and promises the publication of further data which have already been accumulated.

The Atmosphere. By A. J. Berry, M.A. Cambridge: The University Press. 1913.

The advances which have been made in recent years in our knowledge of the chemistry and physics of the atmosphere are described in a very interesting way in this book, which touches upon nearly all the important questions involved in its study. As an introduction the early history and the phlogiston theory are briefly treated, and then the principal constituents of the atmosphere are discussed, short accounts being given of their preparation and properties. In a chapter on modern views on combustion quite recent work is described, and the chapters on the escape of gases from planetary atmospheres and on the probable composition of the atmosphere in early geological time are full of interesting information.

Some Organic Soil Constituents. By Edmund C. Shorey. Washington: Government Printing Office. 1913.

This Bulletin gives a description of the continuation of an investigation, begun some years ago, and reported upon in earlier Bulletins, on the organic matter of the soil. The aim of the research was to isolate and identify the organic constituents contained in that portion of the soil which is soluble in dilute alkali and is not precipitated on acidifying the solution. The soils examined were mostly special specimens which had shown a lack of fertility, either specific or general. The result of the investigation is the isolation of fifteen organic compounds, including one (an aldehyde) not yet identified, thus bringing up the total number of organic compounds isolated from the soil to thirty-five. These substances belong to six classes, including aldehydes, organic sulphur, and organic phosphorus derivatives. The Bulletin is illustrated by photomicrographs of characteristic derivatives of organic compounds isolated from the soil.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Academie des Sciences. Vol. clvi., No. 10, March 10, 1913.

Direct Hydrogenation of Hydrocinnamic Ethers. Preparation of β-Cyclohexylpropionic Acid. — Paul Sabatier and M. Murat.—When the ethers of hydrocinnamic acid, $C_6H_5.CH_2.CH_2.COOH$, are hydrogenated over active nickel at temperatures between 170° and 185° they are totally transformed into the corresponding ethers of β-cyclohexylpropionic acid, $C_6H_{11}.CH_2.CH_2.COOH$. If the temperature is allowed to rise above 200° the results are not good; the hydrogenation leads to the separation of alcohol and acid, which attacks the nickel and reduces its activity. The saponification of the ethers with alcoholic potash gives the potassium salt from which the free acid can be liberated by the addition of dilute sulphuric acid. β-Cyclohexylpropionic acid is a colourless liquid which boils at 2·68°. Its melting-point is 6°.

Chemical Equilibrium in the Action of Hydrochloric Acid Gas on Zinc Sulphate.—Camille Matignon. —In the reaction—

$$(n+1)ZnSO_4(sol.) + 2HCl(gas) = SO_3H_2.nZnSO_4(sol.) + ZnCl_2(sol.)$$

the sulphuric acid set free by the action of the HCl gas on the zinc sulphate would combine with the zinc sulphate to give a solid acid substance. This has been verified by experiment, the composition of the silky needles deposited on cooling being represented by $ZnSO_4.H_2SO_4$. The crystals decompose zinc chloride at the ordinary temperature, and the decomposition may be complete. The

pressure of dissociation may be determined, and hence it may be calculated that at about 12° the pressure of dissociation of the system is normal.

Anhydrous Protosulphides of Alkali Metals.—E. Rengade and N. Costeanu.—The protosulphides of the alkali metals can be obtained by allowing sulphur vapour to react on the fused metal *in vacuo* and then distilling off the excess of metal. The products are white powders at the ordinary temperature, appearing crystalline under the microscope. They turn yellow when heated. The sulphides are thus less coloured than the oxides, and are also much less soluble in the metal. The solubility increases with the atomic weight. The sulphides are more stable than the corresponding oxides, and do not appear to be affected by light nor by anhydrous ammonia. At the temperature at which glass begins to soften they fuse, turning red, and being converted into persulphides with liberation of metallic vapour. They are very readily oxidised. In the cold sodium sulphide is only slowly attacked by air, while the others rapidly deliquesce. When thrown into water they dissolve with hissing and disengagement of heat, but without explosion.

Migration of Chlorine in Halogen Ketone Derivatives.—E. E. Blaise.—The hydrolysis of the oxyisobutyric cycloacetal of dichlormethylketone gives two dihalogen isomeric ketones, differing only in the position of the halogen atoms. Thus, a migration must take place during hydrolysis. The transposition product has probably the constitution $CH_2Cl.CO.CHCl.CH_3$, corresponding to the migration of a chlorine atom from 1 to 3.

MISCELLANEOUS.

Iron and Steel Institute.—*Brussels Meeting, September 1st to 4th*, 1913.—The Autumn Meeting of the Iron and Steel Institute will be held in Brussels, on Monday, Tuesday, Wednesday, and Thursday, September 1st to 4th, 1913. In order that proper arrangements may be made, it is necessary that the number likely to take part in the meeting should be ascertained promptly. The provisional programme of the Meeting is as follows:—

Sunday, August 31.—Secretaries Office opened at the Palais des Académies, Brussels, for the registration of Members' names and the issue of badges and programmes.

Monday, September 1.—Opening Meeting in the Hall of the Palais des Académies. A selection of papers will be read and discussed. In the afternoon visits will be made to places of interest in Brussels. In the evening a Reception will be held by the Burgomaster at the Hotel de Ville.

Tuesday, September 2.—Meeting in the morning for the reading and discussion of papers, at the Palais des Académies. Afternoon visits to Colonial Museum and the Parc de Tervueren. In the evening it is hoped that His Majesty King Albert will be pleased to receive the Members at the Royal Palace, Brussels.

Wednesday, September 3.—A Special Train will leave in the morning for Ghent, where a visit will be paid to the International Exhibition now being held in that City.

Thursday, September 4.—Alternative Excursions will be made to Liége and Charleroi. The Liége Excursion will include a visit to the works of Messrs. John Cockerill and Co., Seraing, to the works of the Ougrée-Marihaye Company, and to the Coppée Coke Oven Gas Plant at Athus-Grivegnée. The Excursion to Charleroi will embrace visits to various metallurgical, glass, and other works in the vicinity of that town.

Celluloid Regulations Bills.—The City of London Celluloid Regulations Bill was thrown out on the second reading on May 28th. The House divided on Mr. Baird's motion for the rejection of the Bill, and the voting was as follows:—For the rejection, 127; against, 47; majority for the rejection, 80. The London County Council then withdrew the celluloid part of their Bill.

The Casting of Magnesium Alloys.—Owing to the affinity of magnesium for oxygen, difficulties arise in casting alloys containing this metal. According to U.S. Patent 1,028,216, of June 4, 1912, Hoffman and Suchy have found that this reaction is mitigated by the addition of a small amount of calcium to the alloy. It is claimed that alloys thus formed may be cast without the formation of either magnesium oxide or nitride, or any other injurious action occurring. For example, magnesium and its alloys, when mixed with from 0·1 per cent to 0·5 per cent of calcium, flow without the occurrence of burning or the formation of a dark skin on the surface of the metal. The castings, moreover, do not effloresce in air and fill the moulds perfectly, and the property imparted by the calcium is not lost on repeated fusion and casting. The calcium may be applied in the form of calcium oxide or may be added during the electrolytic production of magnesium. No characteristics of a calcium alloy are imparted, as the calcium or calcium oxide is used in such small quantities. —*Journ. Ind. and Eng. Chemistry*, iv., No. 10.

Melting-Points of Fire Bricks.—Kanolt (*J. Wash. Acad. Sci.*, ii., 337, No. 14) has determined the melting-points of fire bricks, taking as the melting-point the lowest temperature at which a small brick piece could be distinctly seen to flow. The experiments were conducted in an Arsem graphite resistance vacuum furnace, and the samples, which were from 1 to 2 cm. in diameter, were usually enclosed in a refractory tube to protect them from reducing gas and were heated at the rate of about 10° F. per minute when near the melting-point. The temperatures were determined by means of a Morse optical pyrometer of the Holborn-Kurlbaum type. It was found that in the case of certain bricks made of heterogeneous material of relatively low melting-point, the melting-points were slightly higher after six hours' heating to 1550°, apparently as the result of the gradual running together of dissimilar particles to form a mixture having a higher melting-point than the most fusible of the original materials. The results are summarised in the following table:—

Melting-Points of Fire Bricks.

Material.	Number of samples.	Melting-point °C.
Fire clay brick	41	1555—1725 mean 1649
Bauxite brick	8	1565—1785
Silica brick	3	1077—1705
Chromite brick	1	2050
Magnesia brick	1	2165
Kaolin	3	1735—1740
Bauxite	1	1820
Bauxite clay	1	1795
Chromite	1	2180
Pure alumina		2010
Pure silica		1750

The value 1750° given for silica is not the true melting-point, but represents approximately the temperature at which the silica flows distinctly. It was found that silicon carbide does not melt below 2700°; it becomes unstable at much lower temperatures.—*Journ. Ind. and Eng. Chemistry*, iv., No. 10.

MEETINGS FOR THE WEEK.

WEDNESDAY, 11th.—Biochemical Society, 8.30. (In the Institute of Physiology, University College, London).

THURSDAY, 12th.—Royal Society. "Recent Researches on the Palatine in Relation to Geology, Ethnology, and Physics," by Commendatore Boni. "The Trypanosomes causing Dourine (*Mal de Coit* or *Beschalseuche*)," by B. Blacklock and W. Yorke. "Growth and Sporulation of the Benign and Malignant Tertian Malarial Parasites in the Culture Tube and in the Human Host," by J. G. Thomson and D. Thomson.

FRIDAY, 13th.—Physical, 8. "Some Experiments on Tinfoil Contact with Dielectrics," by G. E. Bairsto. "Method of Measuring the Pressure of Light by means of Metal Foils," by G. D. West.

THE CHEMICAL NEWS.

Vol. CVII., No. 2794.

GREAT ADVANCE IN CRYSTALLOGRAPHY.*

By A. E. H. TUTTON, D.Sc., M.A., F.R.S.

Crystallography has made such remarkable progress during the last few months, and the position at the present moment is so interesting, that it was considered opportune to review it in a Discourse from this historic lecture-table. For, firstly, the descriptions of the crystals of all the ten thousand substances which have ever been subjected to goniometrical measurement have been collected together and classified within the four volumes of a monumental work by Professor von Groth, of Munich. Secondly, this immense labour has been paralleled by the construction, by Professor von Fedorow, of St. Petersburg, of a tabular record of the main crystal elements of all these substances, arranged in a simplified form and with the assurance, which has entailed untold labour to achieve, that they relate to a truly comparative orientation; so that this table is the index to and basis of a new method of "Crystallo chemical analysis," which enables a trained investigator to identify any well-crystallised substance from the result of a brief goniometrical examination. And, thirdly, the whole of these invaluable results have been placed on a firm experimental basis; for the internal structure of crystals, as imagined in all its wonderful details by the greatest geometrical and mathematical minds amongst us, has been revealed on the photographic plate as the result of direct experiment with the excessively minute and all-penetrating wave-motion, or corpuscular energy, of the X-rays.

It is easy to prove that a crystal has an organised structure. The fact is at once revealed by the influence of rapidity or slowness of growth on its character. For example, if a little benzoic acid be melted on a glass plate over a spirit lamp and the plate allowed to cool rapidly in the air, on the object-stage of the projection polariscope, using crossed Nicols, the dark field is almost immediately illuminated by crystals beginning to grow at the margin of the liquid film, and from each bright spot a crystal-needle darts, with fiery tip, like a lightning flash, into the centre of the field, until the whole picture is an interlacing mass of acicular crystals brilliantly coloured in the polarised light, which renders them more visible, the colour being due to double refraction caused by structure. Again, if we crystallise a substance from solution, say potassium bichromate, it entirely depends on whether the degree of supersaturation is slight, the "metastable" condition of Miers and Ostwald, or excessive, the "labile" condition, as to what kind of crystal we obtain. From the metastable solution perfect little single crystals are started into slow growth, by the advent of germ-crystals of the same or an isomorphous substance from the air; while the labile solution spontaneously and rapidly crystallises in the beautiful feathery forms illustrated on the screen. Ammonium chloride and metallic silver afford us even more beautiful screen pictures of arborescent crystallisations, and nothing can exceed the beauty of snow crystals, an example of rapid crystallisation of water-vapour. For goniometry these labile forms are useless, but, nevertheless, they teach us much concerning the structure of crystals. For in them the skeleton, or inner framework and plan of architecture of the crystal is revealed.

It is hard to realise the clearly proved fact that our atmosphere teems with excessively minute crystals—for they possess the complete organisation of a crystal—often not exceeding the one thousand millionth of a milligramme in weight, and capable, whenever they fall into a quiescent slightly supersaturated solution of a crystalline substance of like structure, of calling forth its power of crystallising. In order to be able to exercise this remarkable power, however, the germ crystal must be isostructural in a very strict sense, if not identical with the substance which is set crystallising. Not only must its symmetry be similar, but the dimensions of its structural units—the "bricks" of the crystal edifice so to speak—must be all but identical. The conditions are, indeed, similar to those required for the facile formation of parallel growths of one crystallised substance on another, so admirably investigated by Barker.

Perhaps the most striking cases for the purpose of illustration are those of the rhombic alkaline sulphates, selenates, perchlorates, chromates, or other of the well crystallised salts of the alkali metals potassium, rubidium, and cæsium, and of the base ammonium which is so extraordinarily capable of replacing them. In any such group of salts the periodic law of Newlands and Mendeléeff is most beautifully illustrated by the regular progression of all the properties of the crystals of the three metallic salts, corresponding to the progression in the atomic weights of the metals, the salt of rubidium, the metal of intermediate atomic weight, having invariably intermediate properties, both morphological and optical. A slide showing the gradual slight change in the prism angle of the crystals of the sulphates will make the point clear, the slope of the prism face of rubidium sulphate being intermediate between the greater slope of that of the potassium

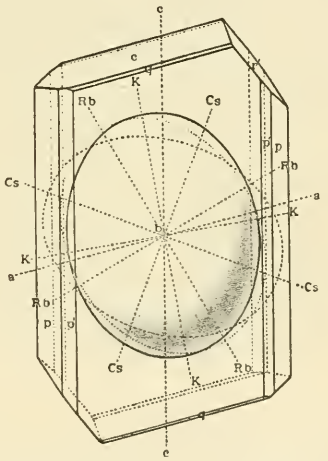


Fig. 1.—Rotation of the optical Ellipsoid of Double Sulphates on replacing Potassium by Rubidium or Cæsium.

salt and the lesser slope of that of the cæsium salt. The variation of the position of the optical ellipsoid in the three monoclinic double sulphates of the $6H_2O$ series containing these three salts is also illustrated by a slide in which the ellipsoid can be rotated through the three positions (the rotation being also indicated in Fig. 1 by the dotted ellipses). In a similar manner the dimensions of the structural units—the molecular volume (that of the "brick" regarded as a molecule) and its expression in the three dimensions of space (which we now have a means of determining, by combining the density and the crystallographic axial ratios, in what are known as topic axial ratios)—vary in regular progression as functions of the atomic weight. Hence, the structural dimensions of the two extreme members of any of these groups of salts, the potassium and the cæsium salts, are most divergent, and Barker has shown that while the rubidium salt will in general form parallel growths with either the potassium or

* A Discourse delivered at the Royal Institution of Great Britain, March 14, 1913.

the cæsium salt, the potassium and cæsium salts themselves will never form satisfactory parallel growths on each other, clearly owing to the disparity in the dimensions of their structural units. Further, the ammonium salt of any group has the interesting property of forming crystals of which the molecular volumes and topic axial dimensions are almost identical with those of the rubidium salt of the same group. Now it is most important and conclusive that the ammonium and rubidium salts form the best of all parallel growths; they form, indeed, no longer merely parallel growths, but zonal growths and complete overgrowths. They also form excellent mixed crystals, and in every way which has yet been experimentally tested they show the nearest approach to true iso-structure. Some photographs of such parallel growths of rubidium and ammonium salts will render the matter clear. There is also one case of iso-structure investigated by Barker, that of calcite and sodium nitrate, which is of particular interest; for these are not chemically isomorphous substances, but they happen to have similar rhombohedral symmetry and almost identical molecular volumes and topic axial dimensions. The slide of parallel growths of sodium nitrate on calcite (reproduced in Fig. 2, by the kindness of Mr. Barker) is very striking and conclusive. Barker has

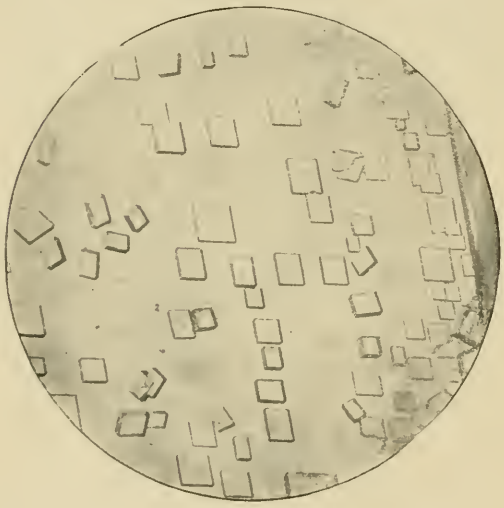


FIG. 2.—PARALLEL GROWTHS OF SODIUM NITRATE ON CALCITE.

recently suggested the nature of the structure of these two substances, two molecules forming the unit "brick," as represented in the slide exhibited. In the case of potassium sulphate and its analogues, one molecule forms the "brick," as represented by the next slide.

It has thus been proved experimentally from the morphological side that a crystal has a definite structure, and that its unit "bricks" or "cells" have definite and measurable dimensions. But the fact is equally well demonstrated optically. We have only to pass a beam of light through a 60° prism of a non-cubic crystal, for instance, quartz, to see at once the radical difference of effect from that given by glass or other non-crystallised substance. For instead of the usual single spectrum produced by glass the quartz prism refracts two distinct spectra, unless it happens to have been cut so that the light traverses the unique direction of single refraction, coincident with the axis of the natural quartz crystallographic prism, which is also the axis of trigonal (threefold) symmetry. The quartz prism used in the experiment is cut at right angles to this direction, so that the axis and refracting edge of the cut prism are parallel to the natural axis, and the separation of the two spectra, corresponding to the two refractive indices of quartz, is thus at a maximum. Moreover, on placing a Nicol prism in the path of the refracted rays, we observe that the light producing the two spectra is oppositely polarised, one spectrum extinguishing when the Nicol has its vibration plane vertical, and the other when the Nicol is rotated so that the vibration plane is brought into the horizontal position. The crystal thus possesses a structure, which is capable of separating a beam of ordinary light into two beams, having definite and perpendicularly different vibration directions.

Again, we see proof of structure if we cut a plate out of the crystal and examine it in a converging beam of polarised light, especially if the crystal, say one of calcite, be cut perpendicularly to the singular axis (or to the bisectrix of the two such axes in the cases of biaxial crystals) of single refraction. A beautiful interference figure is produced, composed of spectrum-coloured rings and a black cross, that is, a figure symmetrical about the axis of trigonal symmetry and of single refraction. This evidence of structure can be most wonderfully reproduced by glass, if we strain the glass by heating and rapid cooling about a cylindrical axis, but an ordinary unstrained piece of glass affords no such effect at all. It is clear, therefore, that the calcite crystal has a symmetrical structure about the axis of single refraction. Similarly, the beautiful biaxial interference figure exhibited on the screen, afforded by a plate of rhombic potassium nitrate, is symmetrical about the centre of the double-looped figure of spectrum-coloured lemniscates.

Sufficient evidence will now have been brought forward that a crystal is endowed with a definitely organised structure. In the crystal of a pure substance we are dealing with a chemical element or compound, and if with the latter it may be of any grade of complexity, from a very simple binary compound to a most highly complicated one composed of a large number of atoms. If the crystal be that of an element the structure is obviously composed of the similar atoms of that element, while if it be a compound we have a structure composed of atoms of as many kinds as there are chemical elements present combined in the substance, and in the same relative proportion as is expressed by the chemical formula of the substance. In the case of a compound, moreover, the structure may also be considered to be that of the molecules of the substance, for they or a simple arrangement of a small number (group) of them form the grosser units of the structure, whilst the atoms are the ultimate units.

Suppose we now represent this molecular or polymolecular grosser structural unit by a point, and that such point be analogously situated within each unit. The essence of crystal structure then is that these points are so arranged in space that if they are joined along the three directions of space by imaginary lines the latter form a "space-lattice" (German, "Raumgitter"), each unit cell of which may be conceived to be the "brick" already alluded to, and the domicile of the chemical molecule or group of molecules (indeed, it is immaterial whether the points are considered as placed at the corners or in the centres of the cells), or, in the case of an elementary substance, of a group of similar atoms. We may therefore define a crystal as follows:—

"A crystal of any definite chemical substance consists of a homogeneous arrangement of grosser units of matter, each consisting of one chemical molecule or a small group of molecules of the substance, and the kind of arrangement is such that these grosser units are all identically (same-ways, parallel-wise) orientated, and that their analogously chosen representative points, one from each such grosser unit, form a space-lattice (Raumgitter)."*

* Since this lecture was delivered (March 14, 1913), and printed by the Royal Institution, a paper by Prof. Theodore W. Richards, of Harvard University, has appeared in the *Journal of the American Chemical Society* for April, 1913 (vol. xxxv., p. 381), in which he shows that his theory of compressible atoms leads to "crystal units" of precisely the molecular or polymolecular character described in this lecture. He supposes such crystal units to be the entities necessary to relieve metastable supersaturation, and their centres to form the points of the crystal space-grating, assumptions with which the lecturer obviously fully concurs.

There are fourteen kinds of space-lattices, slides of several of which are exhibited on the screen. Three possess full cubic symmetry, two are tetragonal, four are endowed with rhombic symmetry, and two are monoclinic; while triclinic, trigonal, and hexagonal crystals have each one space-lattice corresponding to their type of symmetry. In every case it is the full (holohedral) symmetry of the system which is present, no space-lattice possessing merely the lower degree of symmetry corresponding to one of the so-called hemihedral or tetartohedral classes of the system in question.

Now in the solid crystal, not only are the grosser units arranged so that their representative points are repeated in space with extraordinary accuracy of position, with production of unit cells or "bricks" of absolutely identical dimensions throughout the crystal, but the shapes of the grosser units themselves are identically similar and identically similarly orientated in space. Suppose, however, that the force of crystallisation, the directive molecular force concerned in bringing the molecules together in this regular order of marshalling, is only adequate just to attain this marshalling of the grosser units into a space-lattice formation, without being able to fix the units about their own centres of gravity, a certain amount of wobbling about the latter being still permitted. We might, in such circumstances, expect that some of the properties of a crystal, dependent on the space-lattice formation on lines of definite symmetry, such as the optical property of double refraction and polarisation of light, would be developed and exhibited, while the production of exterior plane faces would be either only partial, with rounded edges and the exhibition of plasticity and viscosity, or would not be achieved at all, the objects produced being still fluid. One cause of such a condition of partial success at crystallisation might well be that the substance was composed of a large number of atoms arranged in a long chain, such as the well known "long chain compounds" of organic chemistry, which would offer considerable resistance to marshalling. The author believes that herein lies the explanation of the remarkable "liquid crystals" which Professor Lehmann has made the subject of his particular study, many of which are of just such long chain character.

By the kindness of Professor Lehmann, who has sent over specimens of some of the most characteristic of his substances for the special purpose of this lecture, and of Mr. Poser, of Messrs. Zeiss, who construct an admirably conveniently form of heating microscope and projection arrangement for demonstrating the formation of liquid crystals and their behaviour in polarised light, it is possible to exhibit some of the typical phenomena of these interesting objects on the screen. The substances in question are chiefly such as form two or more polymorphous forms, each stable within a limited range of temperature, and the liquid crystals are usually the second phase observed on allowing the truly liquid heated substance to cool; the liquid crystal phase is produced at a definite temperature during the cooling, and persists through a definite interval of temperature during the continued cooling. It either exhibits distinct attempts at the formation of pyramidal or prismatic crystals, more or less rounded at their edges, as in the case of ammonium oleate shown on the screen (Fig. 3), or manifests itself as doubly refractive and brilliantly polarising drops or streams, such as the drops of para-azoxyanisol, which are set rotating independently by the addition of a little colophonium, as demonstrated in brilliant polarisation colours on the screen; it then suddenly passes with further cooling into the final solid phase, often with the production of brilliantly coloured acicular crystals, as in the case of para-azoxyphenetol exhibited on the screen, or of beautiful star-like or flower-like apparitions, radiating from innumerable centres all over the field, as in the exceedingly beautiful case of cholesteryl acetate. The view here put forth is apparently in agreement with that of Lehmann himself, as most recently expressed both in letters to the lecturer and in a memoir of July 27, 1912, to the Heidelberg Akademie der Wissenschaften, in which he says that in all probability:—"Die Rundung der Formen hänge zusammen mit der Plastizität der Stoffe und habe ihren Grund in unzureichender molekularer Richtkraft, welche wohl genügt, ein Raumgitter herzustellen, nicht aber regelmässige Treppenstufen, wie es nach Hauys Theorie zur Bildung ebener Krystallflächen notig wäre." The formation of regular stepped faces (of invisibly minute steps, "Treppenstufen") the lecturer considers to occur only when the grosser units become fixed about their centres of gravity or representative points, with production of a truly solid crystal.

Fig. 3.—Liquid Crystals of Ammonium Oleate.

But now let us pass to the consideration of the internal

structure of the grosser or space-lattice units themselves. Their symmetry may be, in simple cases, similar to that of the space-lattice, but in general this will not be so. Whatever the stereometric arrangement of the chemical atoms in the molecule may be, and, if more than one molecule goes to form the space-lattice unit whatever their mutual arrangement, and therefore, whatever be the outer configuration of the whole unit, when the crystal is a truly solid one, the force of crystallisation (now no longer denied) is adequate to fix each space-lattice unit, not only considered as a point with reference to its neighbours, but as regards its shape and its whole character, parallelwise and sameways orientated with respect to its adjacent fellows, and as close as possible to them. Also if more than one molecule goes to each space-lattice unit, their mutual arrangement is achieved on a definite plan, and is the same for every space-lattice unit; these constituent molecules of the latter are also as closely packed as possible. The final result is thus to produce an assemblage of chemical atoms, in which not only the demarcation frontier between the space-lattice units disappears, but also that between the constituent molecules in the cases of polymolecular grosser units. We come, ultimately, in consequence, to a structure of atoms, each of which we may represent by a point.

Now, just as the genius of Frankenheim and Bravais revealed to us the 14 kinds of space-lattices, so Sohncke made us acquainted with 65 regular systems of points, including many of the 32 classes of symmetry, but not all, which von Lang had shown crystals to be capable of possessing. Later the number was brought up to 230 by simultaneous and wonderfully concordant geometrical researches by Schönflies in Germany, von Fedorow in St. Petersburg, and Barlow in England, and among these 230 all the 32 crystal classes are represented, and no others.

Hence, we come to the conclusion that the skeletal framework of crystal structure is the molecular or polymolecular space-lattice, and the detailed ultimate structure the atomic point-system. The latter determines the class of symmetry (which of the 32 classes is exhibited) and therefore governs any hemihedrism or tetartohedrism, as the development of less than full systematic symmetry used to be called. But it is the space-lattice which governs the crystal system; that is, which determines whether the symmetry is cubic, tetragonal, rhombic, monoclinic, triclinic, trigonal, or hexagonal, and which also determines the crystal angles and the disposition of faces in accordance with the law of rational indices, the law which limits the number of possible faces to those which cut off small whole-number relative lengths from the crystal axes. Indeed, it is because only those planes which contain the points of the space-lattice are possible as crystal faces that the law of rational indices obtains. For any three points of the space-lattice determine a plane in which similar points are analogously regularly repeated, and which is a possible crystal face obeying the law of rational indices. Moreover, those facial planes which are most densely strewn with points are of the greatest crystallographic importance, being what are known as the primary faces, either parallel to the crystal axes or cutting off unit lengths therefrom, as well as being usually the planes of cleavage.

As the space-lattice units are all sameways orientated, any one atom of the molecular or polymolecular grosser unit might be equally well chosen as the representative point of the lattice, so long as a similar choice were made in every space lattice unit, and the resulting space-lattice would be the same whichever atom were so selected. Consequently, the space-lattice is afforded by the similarly (identically) situated atoms of the same chemical element throughout the crystal structure. The combined point-system (one of the 230 possible point-systems) may thus be considered to be built up of as many identical but interpenetrating space-lattices as there are atoms in the space-lattice grosser unit. These facts are concisely expressed in the definition of crystal structure which was stated as follows by Professor von Groth at the Cambridge meeting of the British Association in 1904·

"A crystal—considered as indefinitely extended—consists of n interpenetrating regular point-systems, each of which is formed from similar atoms; each of these point-systems is built up from n interpenetrating space-lattices, each of the latter being formed from atoms occupying parallel positions. All the space-lattices of the combined system are geometrically identical or are characterised by the same elementary parallelopipedon."

(To be continued).

A STUDY OF THE

FRUIT OF *CRATAEGUS MACRACANTHA*.

By W. BRUCE ARMSTRONG.

THE fruit was gathered in a thorn patch between Mount Vernon and Lisbon, Iowa. This species of the Crataegus grows on shrubs about 15 to 20 feet in height. It is indigenous to the territory from Quebec to Dakota, and as far south as Virginia and Missouri.

We decided to call this species *Macracantha*, although it did not coincide with the description in every detail (according to the classification of Lodd), resembling *Rotundifolia* in a few minor respects. But on account of the difficulties in identifying the species of this genus, it was thought best to name it according to the species which it most closely resembled.

The colour of the fruit is orange bordering on the red. Each apple contains two or three seeds, and the meat is woody. The fruit is about 0·7 cm. to 1 cm. in diameter, and nearly spherical. It was impossible to grind it with a mortar and pestle, and very difficult to cut. The fruit, when burned, gives off an odour resembling that of burning oak leaves, and so irritating as to produce sneezing. At one stage they burned with a distinct sodium flame. This came from the blossom end; they burned with force enough to move them about in the dish. There were about 450 grms. available. The average weight per berry was 0·916 grm.

The Sugars.

About 200 grms. of the fruit were taken for the sugar extraction. They were placed in a litre flask, fitted with an inverted condenser, and treated with successive portions of alcohol for about twenty-two days. The alcoholic extraction was removed each day and a fresh portion applied. When the alcohol was distilled off a thick, almost black, syrup remained. The first extraction was neutral to litmus. But after standing eight days the syrup solution reacted slightly acid to litmus, probably due to fermentation. The colour of the first extraction was dark brown, and it smelled considerably like wet brown sugar. After standing a few hours a light brown sediment settled and the liquid above darkened.

A test with Fehling's solution at the end of twenty-two days showed that the sugars were almost extracted, and distilled water was substituted for alcohol. The berries under the alcohol treatment remained hard, but on the addition of water they became mushy. The last alcoholic extraction was a light yellow colour, but the water was darker than thick maple syrup or vinegar, and smelled like dates which had been boiled in water. The water extraction acted acid to litmus. About twelve days were required to remove all the remaining sugar by the water treatment.

The percentage of the sugars was determined by the Fehling's solution of such a strength that 10 cc. corresponded to 0·05 grm. of sugar. One cc. of the extraction was taken and diluted to 50 cc. with water in a small beaker. This was heated to boiling and titrated with Fehling's solution. The end of the reaction was ascertained by placing a drop of the solution on a folded filter-

paper. The filtrate passes through free from copper oxide to the under side, and the spot is moistened with a drop of a solution containing 10 grms. glacial acetic acid and 1 grm. potassium ferrocyanide in 100 cc. water. On holding up to the light the faintest trace of copper ferrocyanide can be perceived, and the end of the reaction plainly indicated at the first trial. If no colour results, the sugar has not all been reduced. There was found to be 17·98 per cent of sugar.

A portion of the sugar was purified by heating with bone-black for several hours on the water-bath. The purified sugar was almost black even after repeated additions of bone-black. One grm. of sugar, 0·2 grm. pure phenylhydrazine-hydrochloride, and 0·3 grm. sodium acetate and 10 cc. water were mixed in a test-tube, loosely corked, and heated in boiling water. The test pointed to fructose and glucose, both of which were probably present.

The apples, after the sugar was extracted, were dried and weighed. The loss in weight was 63·7 per cent. The apples were black, shrivelled, and hard.

They were finely ground, and treated with ether for the oil.

The Ash.

Several portions of the berries of about 3 grms. each were ashed in a platinum evaporating dish. From one portion iron, aluminium, calcium, and magnesium were determined; from another portion sodium and potassium by a modification of the J. Lawrence Smith method; from a third portion, sulphates; the manganese was determined from a fourth portion by colorimetry; and the chlorine from a fifth portion by titrating with N/10 silver nitrate. As the ash was deliquescent, it suggested the presence of chlorides. A test for phosphates showed their absence. The ash was 2·085 per cent of the berry. The results of the analysis were as follows:—

	Per cent.
Al_2O_3 (trace of iron)	6·86
CaO	13·93
MgO	12·16
K_2O	23·80
Na_2O	37·63
SO_3	3·09
Mn	0·10
Cl	0·15
Total	97·72

The remainder was CO_2.

Acids.

Tests were made according to the wet tests as described in "Knight's Blowpipe Analysis," and showed the absence of both tartrates and oxalates. The acetate test proved acetic acid was present, but this, as before intimated, was probably due to fermentation. Further tests were made which showed the presence of citric acid, but in a very small quantity.

Proteins.

A few berries were crushed and boiled in water. Some of this solution was added to dilute nitric acid and boiled; a yellow colour resulted which when made alkaline with ammonia, turned orange, thus showing the presence of albumin. A portion of the above solution was boiled in lead acetate to which sodium hydroxide had been added until the precipitate first formed re-dissolved. The colour was dark, but not enough to show the presence of sulphur. Some of the dry crushed fruit was heated in a test-tube. Brown fumes were given off. They reacted acid to litmus, but no hydrochloric acid was found.

The nitrogen was determined by the Kjeldahl method. 3·2944 grms. of the fruit were put into a round bottomed flask, and treated with 50 cc. concentrated sulphuric acid and heated until the solution was perfectly clear. It was then diluted to 250 cc. with pure water. Caustic potash was added until alkaline. The solution was poured off and two-thirds of it was distilled into 25 cc. normal hydrochloric acid. This was exactly neutralised with normal sodium hydroxide. There was 0·595 per cent nitrogen.

Oils.

The dried berries, after the sugar was extracted, were finely ground and treated for fifty days with ether. The ether was changed every two days, and the oil obtained by distilling off the ether. The oil was yellowish brown in colour, due most likely to impurities. It was then purified by boiling with bone-black and ether. When pure the oil is transparent, lemon-yellow in colour, and somewhat viscous. It has a peculiar piercing odour akin to that of acrolein. The solidifying point is $-15°$ C. Only 1·5727 grm. were obtained, or about 0·79 per cent oil.

A saponification by Koetstorfer's method was made of the total amount of oil. Two days heating on the water-bath was sufficient to effect complete saponification. The saponification equivalent is 570·3. The saponification was not satisfactory, and the small amount of oil obtained did not permit of another trial; but the high saponification equivalent obtained would indicate either cetyl or myricyl palmitate.

The products of the saponification were separated. The solution was diluted with pure water, and ether added to dissolve the unsaponified oil. This was separated and evaporated to constant weight, which was 0·3069 grm. The indications were that the ether extracted more than the unsaponified oils. The residue was dissolved in hot alcohol and filtered. When the alcohol evaporated a thick oily residue remained.

After separating the ethereal layer the liquid was acidified with sulphuric acid, and heated. In a few minutes the fatty acids liberated by saponification separated out and collected on the top of the solution. They were separated and boiled with distilled water for several hours, separated, and dried on the water bath, and found to weigh 0·1942 grm. Their colour was darker than the original oil, and they smelled very much like machine oil. The amount was so small that nothing could be done to identify them.

To find the weight of the soluble fatty acids the acidified liquid from the above was distilled almost to dryness, and the distillate exactly neutralised with normal caustic soda, using phenolphthalein as an indicator. The washings from the insoluble acids were likewise distilled and neutralised. The distillates were evaporated to dryness to constant weight. The number of cubic centimetres used in the neutralisation was multiplied by 0·022, and the product subtracted from the constant weight. The result was 0·0579 grm. Each apple contains two or three seeds, which undoubtedly contain the oil.

The Alkaloids.

Every available test was made to determine the presence of any alkaloid, but with the exception of two or three, which gave some signs that atropine was present, they were quite unsatisfactory. Out of every known test for atropine only two gave slight evidence of its presence, they were the phenolphtholein test and Wagner's reagent, iodine in potassium iodide.

To the many helpful suggestions and kindly interest of Dr. Nicholas Knight the success of this analysis is due.

Solubility in Water of Lead in Couples and Alloys with other Metals.—Scala Alberto.—It is known that all metals are attacked to a certain extent by distilled water. The action may be simply solution or may be of an electrical nature. The author has performed a series of experiments to investigate the action of distilled water on lead arranged in couples with zinc, tin, carbon, and copper, and on alloys of tin and lead of different compositions, and has found that in no case is the solubility increased by the presence of other substances.—*Atti della Reale Accademia dei Lincei*, xxii., No. 3.

APPLICATIONS OF DUCTILE TUNGSTEN.*

By C. G. FINK.

LESS than ten years ago tungsten was universally conceded to be a very brittle metal. Since the introduction of ductile tungsten (C. G. Fink, *Trans. Am. Electrochem. Soc.*, xvii., 229; W. D. Coolidge, *Trans. Am. Inst. Elec. Eng.*, xxix., 961), however, large quantities of drawn wire, flexible and strong, are being daily produced for the manufacture of incandescent lamps.

We have studied the physical and chemical properties of this new tungsten, and have obtained a number of very interesting results.

The ductile metal is practically insoluble in all of the common acids (W. E. Ruder, *Journ. Am. Chem. Soc.*, 1912, 387), its melting-point is higher than that of any other metal (I. Langmuir, *Trans. Am. Electrochem. Soc.*, xx., 237), its tensile strength exceeds that of iron and nickel, it is non-magnetic, it can be drawn down to smaller sizes than any other metal, and its specific gravity is 70 per cent higher than that of lead.

It was natural that a metal with such striking properties as these should soon find applications other than that for incandescent lamps.

Electrical Contacts.

Wrought tungsten has been substituted with success for platinum and platinum-iridium as contact points in spark coils, voltage regulators, telegraph relays, &c. (W. D. Coolidge, *Trans. Am. Inst. Elec. Eng.*, xxxi., 870; *Journ. Ind. and Eng. Chem.*, iv., 2). The service far exceeds that for platinum and platinum-iridium contacts due to the greater hardness, higher heat conductivity, and lower vapour pressure of tungsten as compared with platinum.

Tungsten Furnaces.

These furnaces are of two types. The type recently described by Winne and Dantsizen (*Trans. Am. Electrochem. Soc.*, xx., 287) consists of an alundum tube wound with tungsten (or molybdenum) wire. To prevent oxidation the tube is encased in an air-tight box with an inlet and outlet for hydrogen. This furnace is admirably well suited for laboratory experiments. Temperatures of 1600°—1800° C. can be easily maintained for hours, whereas platinum at these temperatures would rapidly disintegrate.

A second type of tungsten furnace (U.S. Pat. 1,006,620) is constructed on lines similar to those of the Arsem vacuum furnace. A tungsten metal tube takes the place of the helical carbon resister. The tube is surrounded by a screen and the whole enclosed in an air-tight compartment almost identical to that used by Arsem. The compartment is either evacuated or a small quantity of gas, such as hydrogen, is introduced. This furnace lends itself admirably for the study of reactions at very high temperatures, such as the production of artificial gems.

Tungsten Gauze.

We have used this gauze successfully for separating solids from acid liquors. We performed these experiments on a laboratory scale. However, this gauze could well be used on a commercial scale. For example, for the removal of sludge from copper refining baths, and for centrifugal apparatus, in general, whenever acid liquids or acid gases or dealt with.

Furthermore, it might be used in apparatus such as described by Cottrell (*Journ. Ind. and Eng. Chem.*, iii., 542) for the removal of sulphuric mist from gases. The Cottrell electrodes consist of three concentric cylindrical screens of iron wire, the inner and outer ones acting as discharge electrodes, while the intermediate screen and the outer leaded glass containing vessel act as collecting electrodes from which the deposited acid drains into a leaden pan below. Tungsten gauze is not attacked by sulphuric acid and would consequently give a much longer life than iron gauze.

Wrought Tungsten Targets for Röntgen Tubes.

This application has proved to be one of the most interesting. Tungsten is very well suited for targets or anticathodes, and the realms of application and efficiency of the Röntgen tube have been thereby greatly increased.

As a been shown by Coolidge, the high specific gravity, high melting-point, high heat conductivity, and low vapour pressure make tungsten a far more efficient target than any other metal.

Thermocouples.

We are investigating the thermoelectric properties of the couple, tungsten molybdenum. The electromotive force increases with the temperature up to about 540°, then decreases and passes through zero millivolt at about 1300°. We have found this couple very convenient for high temperature measurements in the tungsten-hydrogen furnace.

Standard Weights.

A material suitable for standard weights must preferably be hard yet plastic, it must not be easily scratched nor marred, but still not be so hard that it will chip or break; furthermore, it must withstand the action of the atmosphere and finally it must be small in bulk. Now wrought tungsten can be made so hard that it will readily scratch glass and still be ductile; furthermore, the density is high (19·3 to 21·4) and it is unaffected by the atmosphere. Tungsten weights remain wonderfully constant.

Tungsten Cells.

We have taken up the study of the electrochemical behaviour of tungsten and have made up a series of cells and combinations. All measurements were made at 25° and compared with the calomel electrode as standard. Our readings for the cell tungsten, aqueous sodium hydrate, potassium chloride, calomel, mercury, are:—

5N NaOH, 0·68; 2N, 0·62; N, 0·57; $^1/_5$N, 0·525; $^1/_{10}$N, 0·50; $^1/_{20}$N, 0·48; $^1/_{40}$N, 0·455; $^1/_{160}$N, 0·445; $^1/_{320}$N, 0·380; and 0·0N, 0·06 volt. In the last cell the tungsten rod was immersed in distilled water.

The addition of small amounts of impurities to the tungsten metal causes the tungsten—sodium hydrate electrode to assume E.M.F. values that approach that of zinc in zinc sulphate.

The values for potassium hydrate are similar to those for sodium hydrate. The E.M.F. of the cell $Hg-Hg_2W_3O_{11}+Na_2WO_4$ solid—Na_2WO_4 sat. soln.—solid Na_2WO_4—W was found to be 0·505 volt and promises to be a good standard cell.

Miscellaneous Applications.

Besides the applications of tungsten cited above, many others have been but partly worked out and others merely suggested.

Owing to its chemical stability the finest sizes of wire down to 0·0002″ or 0·005 mm. in diameter are well adapted for galvanometer suspensions and for cross hairs in telescopes. It has also been suggested to use these fine wires in surgical operations in place of the coarser gold and silver wires. A further suggestion is the use of the wire in musical instruments. The tensile strength and elasticity of tungsten wire are exceptionally high (see table below).

It could be used to advantage in climates where steel is readily corroded.

We are investigating the formation of hydrocyanic acid gas by passing over heated tungsten wire mixtures of nitrogen and acetylene or methane. (Compare Berthelot and Lipinski, *Zeit. Elektrochemie*, xvii., 287).

* Paper presented at the Eighth International Congress of Applied Chemistry, New York. From the *Journal of Industrial and Engineering Chemistry*, v., No. 1.

The heat of formation of HCN is:—$C_2H_2 + N_2 = 2HCN$ −9400 cal. (Wartenburg, *Zeit. Anorg. Chem.*, lii., 299).

We are making acid-proof dishes and tubes out of tungsten. Furthermore, tungsten wire recommends itself as a unit resistance, since it can be made absolutely pure, can be easily duplicated, and is not corroded.

Since tungsten is non-magnetic and elastic it is being tried out in electrical meters, replacing the phosphor-bronze springs.

Similarly watch springs could be made which would never become magnetised. Finally we might mention: tungsten pen points, tungsten drawing dies, tungsten knife blades, tungsten reinforced asbestos curtains, and fire-proof coverings, &c.

Table of Physical and Chemical Properties of Ductile Tungsten.

Density, 19·3 to 21·4.

Tensile strength, 322 to 427 kg. per sq. mm.

Young's modulus of elasticity, 42,200 kilogrms. per square mm. (steel 20,000); *i.e.*, twice as elastic as steel.

Melting-point, 3177 (Langmuir) 3100 ± 60 (v. Pirani and Meyer).

Boiling-point, 3700° (?).

Thermal conductivity, 0·35 grm. cal. per cm. per sec. per 1° (Pt, 0·166) (W. D. Coolidge, *Trans. Am. Inst. Elec. Eng.*, xxxi., 870; *Journ. Ind. and Eng. Chem.*, iv., 2).

Expansion coefficient, $4·3 \times 10^{-6}$ (Pt. $8·8 \times 10^{-6}$).

Specific heat, 0·0358 (Weiss).

Resistivity (25°), hard, 6·2 microhms per cc.; annealed, 5·0 microhms per cc.

Temperature coefficient of resistance, 0·0051 (0°—170°).

Hardness, 4·5 to 8·0 (Mohs scale).

Insoluble in HCl, H_2SO_4, HNO_3, HF, NaOH, KOH, (aq.) $K_2Cr_2O_7 + H_2SO_4$ (C. G. Fink, *Trans. Am. Electro-Chem. Soc.*, xvii., 229; W. D. Coolidge, *Trans. Am. Elec. Inst. Eng.*, xxix., 961). Soluble in mixtures of HF and HNO_3, and in fused nitrates, nitrites, and peroxides.

The boiling-point of the metal has not yet been determined.

The Young's Modulus of Elasticity we determined with a wire 0·00648 cm. in diameter and 784·86 cm. long. The smallest weight (P) was 250 and the largest 1125 grms. The elastic elongation was 0·35 cm. for the smallest weight and 1·65 cm. for the largest. The average for five different weights was 42,200.

The hardness values were determined with the sclero-scope and the values translated into the Mohs scale.

A NEW COPPER ALLOY.

METALLURGISTS all over the country have been very much interested recently in the production of non-corrosive alloys of the various metals. Such alloys are of particular interest to men engaged in chemistry and chemical engineering. The following account of a new copper alloy as given by Robert Grimshaw in a recent issue of the Metal Industry will probably be of value.

In researches made as to the influence of the addition of cobalt to the more important metals, it was found that an alloy of cobalt and tin of about 40 and 60 was especially resistant to acids, even to the most concentrated nitric acid and such as is mingled with chlorides, as, for instance, common salt, which renders it more corrosive, partaking of aqua regia.

As this alloy is exceptionally brittle, hence almost useless where it is necessary to work it, this discovery was almost worthless from the practical standpoint. It was further found, however, that this alloy, dissolved in other metals which better permit mechanical working—as, for instance, copper—gave them a greater chemical resistance. When, for instance, enough of the above mentioned cobalt-tin alloy is dissolved in copper to make alloys containing from 80 to 95 per cent of copper and 20 to 5 per cent of the cobalt and tin, there is obtained a series of alloys which may not only be well filed, bored, turned, forged, &c., but have also a high degree of chemical resistance.

The alloys lying in these series were so little attacked by dilute acids (especially nitric) that the time theoretically required to corrode away a layer of 1 mm. (0·0394 inch) thick was calculated to be five to seven years, even on the assumption that the corrosion would take place at an even rate throughout the entire time. In reality, however, the rate of corrosion diminished, which is readily explained by the fact that where chemical action takes place the more lightly attacked element is removed, while the less soluble remains on the surface and acts as a protective coating.

The preparation of these alloys can take place in the usual manner, but it seems to have been found by the experiments above named that it is best to make the cobalt-tin alloy first and dissolve it in the copper.—*Chemical Engineer*, xvii., No. 2.

THE SCIENTIFIC WEEK.

(From Our Paris Correspondent).

RADIO-ACTIVE MANURES.

M. MARCEL VACHER, Member of the "Conseil Supérieur" of Agriculture, at the last meeting of the National Society of Agriculture communicated the really extraordinary results obtained recently in France at the School of Agriculture of Berthonval, as well as in England at the Agricultural College of Newport, by the employment of certain radio-active manures.

By his studies of the effects of uranium on germination, M. Daniel Berthelot had opened the way. MM. G. Petit, Professor at Alfort, and B. Ancelin, agricultural engineer, undertook some new experiments on March 14th last, and this time using radio-active water and ordinary water for the germination of two distinct groups of seeds of Indian corn. At the end of eleven days the seeds of both groups were germinating; but whilst the radicles of the group treated by ordinary water were not more than 19 cm. in length, the radicles of the group treated by radio-active water reached 94 cm. in length.

At Berthonval and at Newport the radio-active manures have given results not less surprising.

At Berthonval the amount of oats produced per hectare (about 2½ acres) was with ordinary manures 3,400 kilogrms., whereas with radio-active manures it was 3,910 kilogrms.; the produce of sugar beetroots was 19,400 kilogrms. with ordinary manures, and 22,200 kilogrms. with radio-active manures. That is to say, a difference to the profit of radio-active manures of 510 kilogrms. in the first case, and of 2,800 kilogrms. in the second.

Elsewhere the energetic action of radio-activity has been remarked on the vegetation of chrysanthemums, roses, geraniums, and cannas, this action producing a more regular and precocious flowering, and a far brighter colouring of the flowers.

All that seems to promise a new future for agriculture and for horticulture, and is a new process due to the admirable discoveries of M. and Mdme. Curie, of M. Henri Becquerel, and of M. Jean Becquerel, in pursuing such interesting studies on the effects of radium.

STUDY OF BIRDS' FLIGHT AS APPLIED TO AEROPLANES.

In studying birds one can manage to calculate the elements of a monoplane.

For the construction of aeroplanes the data furnished by the study of birds have up till now not been made use of. The wide researches of M. Magnan, Director of the Eçole des Hautes Etudes, on this subject have shown him that it was possible to utilise the figures furnished by nature.

In spite of the considerable differences of weight which separate the bird from the aeroplane, M. Magnan has been able to calculate the dimensions of an apparatus constructed on the model of a bird, and has thus brought a new contribution to this interesting problem.

M. Magnan had shown that the characteristics of the bird vary according as to whether it practises the soaring flight, the flight as with sails, or the flight as if moved by oars. M. Magnan has explained that :—

1. Birds of prey, who generally have a soaring flight, have a large alar surface, a small motor represented by reduced pectoral muscles, a large spread of wing ; rather wide wings and a long tail.

2. Marine birds, who use the sailing flight, possess an alar surface nearly as large as the soarers. Their wing spread is wider whilst their wings are very narrow ; their tail is almost emaciated, their motor is small.

3. The "rowing" birds, such as sparrows, gallinaceous birds, pigeons, &c., offer a very reduced alar surface, with very powerful pectoral muscles, and consequently give very violent movements with their wings. Their wing spread is small, their wing is wide and of a rounded form ; their tail is rather long.

Now the flight of soaring birds is that which most recalls the flight of monoplanes. M. Magnan has searched what would be the dimensions of an aeroplane of this type, copying the characteristics of a hovering bird. He has found for an apparatus transporting 500 kilogrms. :—

Alary surface	14·70 square metres
Weight of wings	98·500 kilos.
Spread of wings	10·50 metres
Width of wing	1·87 metres
Length of tail	2·06 metres
Length of apparatus ..	4·67 metres

Two important remarks are :—

1. By the formula employed by M. Magnan one has the advantage of calculating exactly the dimensions of a monoplane according to the weight that it must carry in its flight.

2. The monoplanes in use are too long in comparison to one that would copy a soaring bird. The other dimensions are nearer than might be supposed to those calculated after the data furnished by nature.

Production of Aluminium.

At the present time France produces as much aluminium as Austria, Germany, and Russia together, and comes, from this point of view, immediately after the United States.

The following table (in tons) drawn up in 1911 by M. Trillot, on the occasion of the International Exhibition, of Liège, is a proof of this assertion :—

Years.	France.	England.	Cent. Europe.	U. States.	Total.
1899	800	600	1,600	5,000	8,000
1900	1,000	600	2.500	3,200	7,300
1901	1,200	600	2,500	3,200	7,500
1902	1,400	600	2.500	3,300	7,800
1903	1,600	700	2,500	3,100	8,200
1904	1,700	700	3,000	3,700	9,300
1905	3,000	1,000	3,000	4,500	11,500
1906	4,000	1,000	3,500	6,000	14,500
1907	7,000	2,500	4·500	7,000	21,000

For 1911 the total production of France reached 14,700 tons, and the production of the whole world 32,000 tons at the most. The advance of France has then been largely kept up during the last four years.

The regular increase of this production may be considered as quite remarkable when it is remembered that in 1878 France produced only 1 ton of aluminium. It is true that in 1857 the works installed at Nanterre under the direction of Sainte-Claire Deville had been able to put out 600 kilogrms. at 97 per cent of pureness ; but the metal which contained 2·7 of iron and 0·3 of silica was unfit for the industrial uses such as they are understood to-day. It was, then, the year 1878 which saw the real birth of the modern industry of aluminium.

At any rate, in 1800 the world's consumption reached 1500 kilogrms., produced by the one French manufactory of Salindres. From 1886, when the purely chemical methods were abandoned for the electrolytic method, the production went on increasing gradually, and in 1896 reached 1755 tons.

Not less interesting is the descending progression in the sale price. Until about 1856 the kilogrm. of aluminium cost from 900 to 1000 francs. The works of Sainte Claire Deville quickly reduced its market value to 300 francs per kilogrm., and this price has since then continually decreased as the manufacture was improved.

It was only 100 frs. in 1885, when the adoption of electrolytic processes precipitated the lowering of its price, which was only 80 frs. in 1886, and fell to 25 frs. in 1887 ; in 1888 to 15 frs., in 1892 to 12 frs.

According to a reliable statistic, the variations it has undergone since then are the following :—

Years.	Price per ton, £.
1892	495
1896	163
1901	130
1905	130—170
1907	200—106
1908	100— 65

The average price per kilo., which was 2·60 frs. in 1900, passed to 3·25 frs. in 1901 to fall to 2·80 frs. in 1903, rising again to about 4·70 frs. in 1907, but in 1908 it was only 2·15 frs. At the end of 1908 the price of the kilogrm. even went considerably beneath 2 frs.

This progression has not stopped, and there is every reason to believe that it will not be stopped for some time to come. But it is not only in France that this progress is to be noticed ; according to a recent official publication, the United States have increased their extraction of bauxite from 149,932 tons in 1910 to 155,618 tons in 1911, with a global value of 3,900,000 frs., being an increase of 178,800 frs. on the preceding year.

These figures show how artificial was the crisis of 1908-1909, and they show how great is the ever increasing prosperity of the young and great industry which produces metallic aluminium.

The Earth's Continental Pole.

M. Alphonse Berget, Professor at the Oceanographic Institute, has just made a series of very interesting studies in order to find the position of the Continental pole of the earth.

If we take for the pole a little French island, the Isle of Dumet, situated near the mouth of the river Vilaine, we can trace a large circle, which divides the earth into two hemispheres in such a way that one contains almost the totality of continents, 45·5 per cent land and 54·5 per cent water ; that is the *Continental hemisphere*, whereas the other, the *Oceanic hemisphere*, contains 88·7 per cent water and only 11·3 per cent of emerging land.

So, then, the Isle of Dumet, according to the successive trials and precise measurements of Prof. Berget, is the Continental pole of the earth. Any other point gives two hemispheres, of which the differentiation between terrestrial and marine domains is less marked.

The Falling op Leaves and Rain.

A meteorologist of Auxerre, M. David, had wondered if there exists a relation between the precocity of the falling of the leaves from the trees and raininess. His observations have especially dealt with the lime trees on avenues, which can only draw their nourishment at a certain depth. From the observation of a dozen years he concludes that the meteorological circumstances of the summer are not always sufficient to explain the fall of leaves,

When the winter has been sufficiently damp to assure reserves in the deep layers of the soil, it seems that the foliage has nothing to fear from heat and drought. It suffers more from the cold. Premature frosts accelerate very decidedly the fall of the leaves.

The different vegetable species are also very differently influenced. Thus in 1907, in spite of the provision of water in the sub-soil, the lime trees lost their leaves two months before the plane trees and the fruit trees. The relations between the climatic conditions and the fall of the leaves of trees are very complex.

The Large Cetacea are Disappearing.

Like the elephant of the Black Continent, which will be totally exterminated by ivory hunters in seven or eight years' time, the whole of the other large cetacea living in the sea off the east coast of Africa will, if care is not taken, certainly disappear in a still shorter time, and that to the great detriment of the public fortune. Such is the cry of alarm uttered by M. Perrier, Director of the Paris Natural History Museum.

Several years ago M. Gruvel, during his explorations on the African coast, had remarked the prodigious abundance of large cetacea: Narwhals, dolphins, porpoises, and spermaceti whales. He had called the attention of the Government and of French industry to these enormous riches, but the matter was not taken up, and no attention was given to his reports on this interesting question. And to-day more than thirty companies are engaged in the fishing of the large African cetacea.

To give an idea of the enormous quantity of marine animals thus destroyed, it is to be remarked that all these companies are making profits varying from 20 to 400 per cent. Now for the crew of a whaler only to cover their expenses they must capture from 100 to 150 cetacea.

M. Perier declares that unless, in a brief delay, an international convention interferes to put a break upon these hectacombs there will not be a single cetacean left on the African coast in two or three years' time.

One of Rubens' Pictures Identified by Photography.

Prof. Lippmann announced, a short while ago, that photography had been able to reproduce the traces that had become invisible to the naked eye, of retouchings made by Raphael on a certain number of his drawings.

By the use of a similar process, and by projecting a cone of ultra-violet rays on a picture attributed to Rubens, M. Parenty, Chief Engineer of the State Manufactories of Lille, has been able to identify the work of the great master.

This picture of the Museum of Lille is a decollation of Saint John the Baptist, which was marked as attributed to Rubens. M. Parenty, on a photographic negative of this picture, has been able to show up very distinctly the authentic signature of the illustrious master. This signature having become completely invisible, had up till now not been discerned by connoisseurs.

Valuation of Flours.—Eug. Rousseaux and Maurice Sirot.—The ratio of total nitrogen to soluble nitrogen in flour may be found by determining the total nitrogen by Kjeldahl's method, and treating 10 gr. of the flour with 150 cc. of water on the water-bath, cooling, shaking, and filtering. The nitrogen is then determined in 50 cc. of the filtrate, corresponding to 2·5 gr. of flour. For good samples the ratio is about 5·72. If it falls below 5·2 the flour is inferior, and conversely for a flour to be good its ratio $\frac{\text{total nitrogen}}{\text{soluble nitrogen}}$ must be about 5·7, whatever the acidity, which is sometimes low in bad flours. The determination of the ratio enables chemists to form an opinion as to the value of a flour submitted to them for examination.—*Annales des Falsifications*, 1913, vi., 52.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, May 29th, 1913.

Sir ARCHIBALD GEIKIE, K.C.B., President, in the Chair.

PAPERS were read as follows:—

"Acineta tuberosa: *A Study on the Action of Surface Tension in Determintng the Distribution of Salts in Living Matter.*" By Prof. A. B. MACALLUM, F.R.S.

In previous investigations it was found that the salts demonstrated micro-chemically to occur in the living cell were not uniformly diffused, but were condensed or "localised" at points in its cytoplasm or at parts of its surface. Amongst such salts were the compounds of potassium, which are very soluble and are not known to form precipitates in nature. It was concluded that some other force than simple osmotic pressure was concerned in this distribution of the salts, especially in the cases where the condensations were in those portions of the cell surface where, from the deformation observed, it was inferred that a lowering of surface tension was involved. The explanation advanced was that surface tension was the factor primarily concerned in these condensations.

Two years ago an investigation of the distribution of potassium salts in *Acineta tuberosa*, a marine Suctorian Protozoan, gave results which appear to place the matter beyond doubt.

In this form the potassium salts are distributed only (*a*) in the surface films of the tentacles which are extended to capture other organisms as food; (*b*) at the interface between the cytoplasm of the cell and the young germ bud (when present); and (*c*) at the interfaces between the cytoplasm and certain minute spherules contained in it. The rest of the cytoplasm, except in certain instances to be mentioned, appeared free from potassium, although the reaction used to demonstrate its presence is sensitive enough to reveal, in the test-tube, a concentration at least of 1 of potassium in 300,000 of water.

When the tentacles begin to retract, the potassium salts in their films diffuse into the cytoplasm immediately below the films and, as retraction proceeds, into the cytoplasm of the main body of the organism. When complete retraction obtains, all of the potassium originally present in the films of the tentacles is now diffused, not uniformly, throughout the cytoplasm. As extension and retraction of the tentacles are to be regarded as due to alterations of the surface tension of their films, it would follow that the condensation of potassium salts in the latter is a surface tension effect, and that surface tension brings about the condensations at the interfaces in the cytoplasm and between the latter and the young germ bud.

It is possible that potassium lowers the surface tension at the points indicated, but extension may take place in its absence as in fresh water Suctoria (*e.g.*, *Tocophrya quadripartita*). In the films of the tentacles, and more especially of their capitate ends, fats have been observed, and these may decrease the surface tension, but the diminution of the latter may be due to amino acids produced by enzyme action on the proteins of the tentacles.

The potassium salt of the organism appears to be derived from its food, not directly from the sea-water. It is apparently in greater concentration in the films of the tentacles than in the sea-water into which it should, but does not, quickly diffuse. It would seem, therefore, that surface tension not only determines the condensations in the films and elsewhere in the organisms, but maintains these condensations against the forces of diffusion.

"*Morphology of Various Strains of the Trypanosome causing Disease in Man in Nyasaland.* IV. *The Mzimba Strain.*" By Surgeon-General Sir DAVID BRUCE, F.R.S.; Majors D. HARVEY and A. E. HAMERTON, and LADY BRUCE.

"*Notes on* Toxoplasma gondii." By HELEN L. M. PIXELL, B.Sc.

"*Investigation by Pedigree Breeding into the Polymorphism of* Papilio polytes, *Linn.*" By J. C. F. FRYER.

"*Action of Radium Rays upon the Cells of Jensen's Rat Sarcoma.*" By S. RUSS, D.Sc., and HELEN CHAMBERS, M.D.

SOCIETY OF CHEMICAL INDUSTRY.
(LONDON SECTION).

Ordinary Meeting, June 2nd, 1913.

Prof. W. R. HODGKINSON in the Chair.

THE following papers were read and discussed :—

"*Precipitation in Aqueous and Colloidal Systems.*" By W. P. DREAPER.

Experiments are recorded which deal with the precipitation of insoluble compounds within glass capillary tubes, thus overcoming disturbing influences of cross currents, &c. For example, a 2 per cent solution ol barium chloride is drawn up into a capillary tube, and one end sealed. The tube is then placed into a horizontal position, and inserted in a larger one, containing 5 per cent K_2SO_4. Barium sulphate is precipitated in the tube, and stratification effects are obtained similar to those previously observed in the presence of added colloids. Similar results have been obtained with lead chloride and other lead salts. In the former case crystals of lead chloride have been obtained having a length of 1·5 mm. When precipitating barium sulphate in such tubes in the presence of 2 per cent gelatin, the barium sulphate is first precipitated in an extremely finely divided condition. On the entrance of further K_2SO_4, this same precipitate becomes strongly crystalline, and the area becomes transparent.

A similar result is not obtained when $BaCl_2$ or NaCl replaces K_2SO_4, so that the further change in crystalline state is not due to the action of an electrolyte as such.

Stratification may thus be obtained in the absence of gels, in tubes up to 1 mm. diameter, and it is thus confirmed that the presence of certain banded mineral deposits in nature may be due to the reaction taking place through a porous mineral deposit, in which the interstices may correspond to the above conditions, rather than to the actual presence of a gel, and that crystals of silica, &c., may have formed under such general conditions as those indicated. Changes in physical state may occur *in situ* in the dyeing of fibres, setting of cements, &c., and account for certain observed phenomena. The experiments are being extended to sols as well as gels, and to other solvents besides water.

"*Some Experiments on the Theory of Electro-tanning.*" By E. K. RIDEAL and U. R. EVANS.

Electro-tanning processes have hitherto been largely empirical. Some attempt has been made in these experiments to determine the nature of the forces at work, and so discover the conditions which will ensure quick transfer of the tan substance at a low expenditure of electrical energy and tan material.

Three modes of transfer of dissolved tanning matter are possible, (1) ionic conduction, (2) cataphoresis, (3) electric endosmose. Additions of acids and salts will affect all these modes of transfer; in addition, they will "reduce the proportion of current in the useful work of tannin transference by increasing the conductivity as a whole," and will increase the tendency to polarisation. The nature of the electrode material will have an important effect upon the electrodic decomposition of the tannin substances.

Experiments in cells divided by porous pots showed that with copper electrodes there is more cathodic, but less anodic, decomposition than when carbon electrodes were used. Marked endosmotic transference of the liquid occurred; but the solvent only carried the tannin matter with it in the absence of dissolved salts.

The majority of experiments were conducted on the passage of tannin solution (with or without additions) through glass tubes filled with jelly impregnated with very dilute ferric chloride. The appearance of the "ferric tannate" colour afforded a means of following the migration of tannin through the tube. A large number of such tubes were kept under observation for several days continuously, various additions in varying amounts and different voltages being used in the different tubes. In some cases, for comparison, no E.M.F. was applied. The conclusions to be drawn were :—

1. The application of a current has a marked accelerating action on the diffusion of tannin; this is all the greater the greater the voltage.

2. The greater part of the transfer is due to ionic or cataphoretic movement in the "positive to negative direction"; part is due to endosmose in the opposite direction.

3. The addition of strong acids and ionising salts is objectionable. They show in no case any marked specific accelerating effect of the tannin transference at a constant E.M.F., and as they increase the conductivity of the solution as a whole they decrease the transfer per kilowatt hour, besides causing an unnecessary electrolytic attack upon the electrodes.

4. Weaker acids are less objectionable, but should be kept as low as is consistent with the production of good leather. Their formation by fermentation is avoided by keeping the bath sterile; their formation by electrolytic splitting of tannins is minimised by the suitable choice of electrode material. In general, carbon cathodes and copper anodes will be best; but if for purely "tanning reasons" the presence of weak acids is desired, then carbon anodes may be used, although in this case the electrodic loss of tannin matter may be greater.

"*An Illustration of the Partial Pyrite Process.*" By W. R. SCHOELLER.

True pyritic smelting can only be applied to massive sulphide ores. Silicious ores are treated by the partial pyrite process in which 5—12 per cent of coke is added to the charge. Ores of the latter class are widely distributed, and the process under discussion may be used with advantage to effect a concentration of gold and silver in a matte which is usually poor in copper.

An example of the application of the process at a South American smelter is given. Scarcity of water and fuel prevented concentration or roasting; the ore was smelted in its raw state with dolomitic limestone and 8 per cent of coke, giving a bisilicate slag low in iron and high in magnesia and alumina. Yet it gave no trouble, as it ran freely and the losses in values were small. The matte assayed 10—15 per cent of copper; the concentration attained was 3·5 : 1.

"*Estimation of Alcohol in Beer by means of Malligand's Ebullioscope.*" By J. C. CAIN.

The estimation of alcohol in beer and wine by means of Malligand's ebullioscope has been applied to the cases of French wines and German and Scandinavian beers, but no results have hitherto been published with regard to English beers.

The author shows that the amount of alcohol by volume in English beer, determined either by Malligand's ebullioscope or by the official distillation method, is the same within the limits of experimental error.

The alcohol content of a number of English beers was determined and found to vary from 3·75 per cent in the case of a "family ale" to 8·8 per cent in the case of a "Burton draught ale."

"*Joint Action of Catalysing Agents. Dehydration of Ethyl Alcohol and Ethyl Ether.*" By General W. IPATIEW.

This is a claim for priority in respect of the reactions described by Dr. C. Sprent in a paper communicated to this Section earlier in the year.

NOTICES OF BOOKS.

Osmotic Pressure. By Alexander Findlay, M.A., D.Sc., F.I.C. London, New York, Bombay, and Calcutta: Longmans, Green, and Co. 1913.

The editor of this excellent series of monographs on inorganic and physical chemistry is responsible for this book, which advanced students who are specialising in either branch of the subject will find a valuable addition to their text-books. The treatment is exceedingly clear, and no great mass of detail is allowed to obscure the main issues. The author exhibits perfect impartiality in putting different views before his readers, while at the same time he makes it quite clear what his own opinions are. The experimental work which has been done by the American school of investigators is well summarised, and the modern type of cell is described and illustrated. Theoretical questions are treated fully, and the criticisms which have been levied against the osmotic theory and the thermodynamical treatment of the problems involved are well discussed and answered. The general theory of ideal solutions to which very little attention has quite inexplicably been paid is also clearly treated, and views regarding the cause of osmosis are fully explained.

The Manufacture of Sulphuric Acid and Alkali. By George Lunge, Ph.D. Fourth Edition. Volume I., Parts I.—III. London: Gurney and Jackson. 1913.

The ten years that have elapsed since the publication of the last edition of this treatise have seen great advances and extensions in the industries of which it treats, and the fourth edition has had to be greatly enlarged. Book I., which is issued in three separate volumes, treats of the preparation and properties of sulphuric acid, and gives a most minute and detailed account of the raw materials, the process of manufacture, recovery of nitrogen, purification and concentration of the acid. The author gives his readers the benefit of his very wide experience of sulphuric acid manufacture, and has also brought together all the material on the subject which is to be found in technical literature, patent specifications, &c. In the addenda quite recent information, published while the book was in the press, is included, so that the text has been brought down to the latest possible date.

The Chemistry of Dyeing. By John K. Wood, D.Sc. London: Gurney and Jackson. 1913.

Advanced students in technical colleges as well as practical men engaged in the dyeing industry will find that this book gives a satisfactory summary of the chemistry of dyeing, and the author has undoubtedly made the best use of the limited space at his disposal. The reader is supposed to be familiar with the elements of physical chemistry and to have a fair knowledge of general chemistry, and the author limits his task to the explanation of the application of their principles to the process of dyeing. If the student has the time and opportunity to look up the copious references to the literature of the subject given in the bibliography he will get a thorough knowledge of the theory of dyeing. The accounts of textile fibres and of the general properties of different classes of dyes are necessarily slight, but there appear to be no omissions of importance. Theories of the nature of dyeing are treated in rather more detail, the author advocating the view that the process has the dual character of absorption and fixation.

Chemistry of the Oil Industries. By J. E. Southcombe, M.Sc. London: Constable and Co., Ltd. 1913.

This book is intended to fill the gap between elementary text-books of pure chemistry, from which the reader can usually obtain only a very slight knowledge of the chemistry of the animal and vegetable oils and fats, and the comprehensive treatises in which the subject is discussed in minute detail. The author concerns himself chiefly with the technology of the oils and fats, and their industrial applications are given full consideration. Analytical methods are also described, and at the end of the book there is a good summary of the problems in oil chemistry now attracting special attention. Some space is wasted in discussing the elements of organic chemistry which could quite well be found in a general text-book, but on the whole the author has selected his material well, and produced a book which is a useful introduction to the larger works on the oil industries.

The Chemistry of Steam-heated Soils. By Oswald Schreiner and Elbert C. Lathrop. Washington: Government Printing Office. 1912.

This bulletin contains a report of a series of experiments on the chemical changes produced in soils which have been subjected to steam heating, as in the process of sterilisation. Some of the results obtained simply corroborate those of earlier investigators of the same problems; thus the formation of both beneficial and harmful compounds has been proved by workers who have performed cultural tests. The authors have isolated many of the compounds formed, and have shown that most of those which are beneficial are decomposition products of the nucleic acid present before heating. Dihydroxystearic acid is increased in quantity when previously present and produced, when previously absent, by the heating process. It has a harmful effect upon plant growth, and it more than counterbalances the good effect of other compounds formed. After it has been eliminated or diminished by oxidation, cropping, liming, or the use of nitrates, the beneficial effects of steam-heating become apparent.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clvi., No. 11, March 17, 1913.

Hertzian Oscillations produced by Intermittent Discharges from Isolated Spots of the Cathode in a Crookes Tube.—Kr. Birkeland.—A cathode in a discharge tube fed by a continuous current emits every second, in certain conditions, hundreds or thousands of beams of cathode rays separated by intervals determined in each case by the experimental conditions. If a large magnetic globe cathode is used these eruptive discharges may become very violent, while if the cathode is rendered incandescent and the electrodes are made the poles of a primary circuit, violent oscillations are produced. At the same time long luminous threads are seen coming rapidly from the points of eruption of the cathode, and are reflected from the anode just as a ray of light is reflected by a mirror. The cathode is very sensitive to magnetic forces, and telegraphic signs can be transmitted by its magnetisation.

Quantitative Study of the Absorption of Ultra-violet Rays by Acetone.—Jean Bielecki and Victor Henri.—Acetone in solution and in the liquid state possesses a single band in the ultra-violet; the maximum is at 2706 in alcoholic solution and at 2648 in aqueous solution. The theoretical absorption curve and that obtained experimentally very closely resemble one another between 2405 and 2981. About 1 molecule in 40 intervenes in the absorption.

Dissociation of Gaseous Compounds by Light.—Daniel Berthelot and Henry Gaudechon.—There is a remarkable parallelism in the decomposition of gaseous compounds by heat and light. Those gases which are decomposed at a moderate temperature are similarly

affected by radiations of medium frequency, and, in general, the vibratory frequency corresponds to the photochemical temperature. Decomposition by light, as well as that by heat, is generally reversible, but re-combination may be hindered by passive resistances, and the equilibrium is sometimes so pronounced that the reaction appears total. From experiments with the first two families of the metalloids it appears that the stability of the hydrogen compounds to light (and to heat) decreases as the atomic weight increases.

Equilibrium between Lead Chloride and Ammonium Chloride in Aqueous Solution.—N. Demassieux.—From the equilibrium curves of lead chloride and ammonium chloride in aqueous solution it is seen that the double salt, $2NH_4Cl.PbCl_2$, can only exist in aqueous solution at temperatures above 70°. The two branches of the curves corresponding to lead chloride and to the first double salt, $2PbCl_2.NH_4Cl$, cut at the eutectic point at an angle which is practically 0°, and the general direction of the curve at this point is horizontal.

Synthesis in the Indigoid Group.—A. Wahl and P. Bagard.—Isatin and thioisatin behave differently towards oxindol in the same conditions, and 1-methylisatin resembles the former, yielding 1-methylisoindigotine. The condensation of *o*-methylisatin with oxindol in acetic solution containing aqueous HCl gives isoindigotin, but in an anhydrous medium indirubin is obtained practically quantitatively. This is a new synthesis of indigotin which occurs in the cold, is instantaneous, and gives a very good yield.

Action of Hydrochloric Acid on Sulphonic Quinone.—A. Seyewetz.—Hydrochloric acid transforms sulphonic quinone into chlorinated sulphonic hydroquinone, when the temperature is not raised above 20°. Above this temperature HCl either eliminates the sulphonic group and gives monochlorhydroquinone, or else replaces this group by chlorine and gives dichlorhydroquinone.

Atti della Reale Accademia dei Lincei.
Vol. xxii. [i.], No. 3, 1913.

New Derivatives of Azoxybenzene.—A. Angeli and Bruno Valori.—The oxidation of *p*-azobenzene carboxyllic acid by means of hydrogen peroxide gives β-azoxybenzene carboxyllic acid, which may be reduced to an azo-acid by zinc in acetic acid solution. The authors have prepared the ethyl ether of the acid and also its bromine derivative. Some α-azoxy acid is also formed during the oxidation, and may be separated by the addition of acetic acid and cooling. *p*-Azobenzene sulphonic acid, $C_6H_5.N:N.C_6H_4SO_3H$, similarly yields an azoxy acid when treated with hydrogen peroxide, and trinitroazobenzene gives an asymmetric trinitro azoxybenzene.

Reduction of Sodium Nitroprussiate by means of Sulphuretted Hydrogen.—Domenico Venditori.—The action of sulphuretted hydrogen on sodium nitroprussiate gives rise to a solution and an insoluble substance. The solution yields crystals of $Fe_4(NO)_7S_3Na.2H_2O$ on evaporation, and also sodium ferrocyanide, while the insoluble substance contains iron, cyanogen, sodium, and water in the proportions $5Fe : 16CN : 3Na : 6H_2O$. Thus the action is very different from the reduction of potassium ferricyanide by means of H_2S, which has already been studied, and the presence of the NO group profoundly modifies the behaviour of the salt.

MISCELLANEOUS.

Anglo-German Exhibition, Crystal Palace.—On June 11th the Right Hon. the Lord Mayor of London officially opened at the Crystal Palace the Anglo-German Exhibition. This Exhibition, although a small one, is of a very important character, for not only does it fill another year of exhibition life in the history of the famous old Crystal Palace, but it also puts forward at a very seasonable time the right hand of fellowship to our German cousins. In spite of innumerable difficulties, the management of this most laudable enterprise has prepared a programme calculated to please all visitors to this historic building, famous from the year 1851. It is to be sincerely hoped that June 11th will prove to be a very important day both in the history of the famous old Crystal Palace, and also in marking the beginning of more friendly feelings towards that Power so nearly allied, if not in matters of politics, yet in blood relationship. Visitors to the Anglo-German Exhibition can from June 11th look forward to a most pleasurable visit to the Crystal Palace. Good music and a most varied programme of in and outdoor attractions and summer sport in all its forms, together with such exciting up-to-date novelties as a balloon race and a large and select variety of amusements have been arranged. Anglo-German Art will, without doubt, be one of the principal attractions of this Exhibition, and a fine collection of pictures from some of the best known and most distinguished artists of the two countries will be on view. The different styles adopted by the artists will be of great interest to those visiting this section. There will also be a fine exhibit of modern sculpture, including forty to fifty works of the most striking character. One of the most novel exhibits which can be seen in the great Canadian building in the Exhibition grounds will be a wonderful display of the Anglo-German posters, demonstrating the advance made in both countries in this most necessary method of pictorial advertisement. The promoters also are endeavouring to secure the co-operation of a well-known firm (who undertake this most important work) to furnish a live exhibit, and to enable visitors to view the poster in its making through all its varied stages. Every effort has been made to study the comfort of the public, and, in addition to an improved railway service, a most efficient motor-bus service has been secured running from North London, through the West End, and South London to and from the Crystal Palace.

MEETINGS FOR THE WEEK.

Wednesday, 18th.—Microscopical, 8. "The Measurement of Working Aperture" and "A Method of Investigating Diatom Structure," by H. Hartridge. "The Higher Bacteria (Sphærotilus)," by E. Moore Mumford. "The Structure of the Nucleus," by E. J. Sheppard.

Thursday, 19th.—Royal Society. "Atomic Specific Heats between the Boiling-points of Liquid Nitrogen and Hydrogen—I., The Mean Atomic Specific Heats at 50° Absolute of the Elements a Periodic Function of the Atomic Weights," by Sir James Dewar. "An Active Modification of Nitrogen produced by the Electric Discharge," by Hon. R. J. Strutt. "On the Electrical Emissivity and Disintegration of Hot Metals," by J. A. Harker and G. W. C. Kaye. "On a Method of Measuring the Viscosity of the Vapours of Volatile Liquids, with an Application to Bromine," by A. O. Rankine. "Efficiency of Selenium as a Detector of Light," by E. E. Fournier d'Albe. "Synthesis of the Anhydrides of α-Aminoacyl Glucosamines," by A. Hopwood and C. Weizmann. "Flexure of Telescope Mirror-discs arising from their Weight, and its Influence upon Resolving Power," by H. S. Jones. "Condition that a Trigonometrical Series should have a certain Form," by W. H. Young. "Trigonometrical Series whose Cesaro Partial Summations Oscillate Finitely," by W. H. Young.

— Chemical, 8.30. "Absorption Spectra and Chemical Reactivity—Part III., Trinitrobenzene, Trinitroanisole, and Picric Acid," by E. C. C. Baly and F. O. Rice. "Derivatives of *o*-Xylene—Part V., 5-Bromo-*o*-4-Xylenol and 6-Bromo-*o*-4-Xylenol," by D. J. Bartlett and A. W. Crossley. "Rotatory Dispersive Power of Organic Compounds—Part III., The Measurement of Magnetic Rotatory Dispersion; Part IV., Optical and Magnetic Rotatory Dispersion in some Simple Organic Liquids," by T. M. Lowry. "Action of Ozone on Cellulose—Part IV., Cellulose Peroxide," by C. Doree. "Isomerism of *p*-Azophenol," by P. W. Robertson. "Sylvestrene—The Constitution of *d*-Sylvestrene and its Derivatives," by W. N. Haworth, W. H. Perkin, and O. Wallach. "Synthesis of Pinacones," by W. Parry. "Refractivities of Acenaphthene and its Monohalogen Derivatives," by H. Crompton and W. R. Smyth.

THE CHEMICAL NEWS.

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GREAT ADVANCE IN CRYSTALLOGRAPHY.*

By A. E. H. TUTTON, D.Sc., M.A., F.R.S.

(Continued rom p. 280).

Having thus arrived at a comprehensive idea of crystal structure on the assumption of each atom and each grosser space-lattice unit being only a point, as far as which we are on safe and assured ground, we may proceed to the consideration of the various ideas advanced concerning the character of the units of structure thus represented by points, that is, concerning the mode in which the space around the point is more or less filled up.

The valency theory of Barlow and Pope considers the atomic point to be expanded into the sphere of the atom's influence, the relative size of which in any one substance is supposed to be proportional to the fundamental valency of the chemical element of which the atom is composed. The spheres are further assumed to be pressed together on crystallisation until they fill space, becoming thereby deformed into polyhedra. The theory of von Fedorow, on the other hand, considers the grosser or space lattice units to be parallelohedra; besides those corresponding to the 14 space-lattices there are 9 other parallelohedra (making 23 in all) composed of simple Sohnckian point-systems compounded of interpenetrating space lattices. All the 23 parallelohedra are arranged parallelwise, and fill space without interstices. There are, however, only four types, namely, the cube, the rhombic dodecahedron (which has a second vertically elongated variety), the cubo-octahedron, and the hexagonal prism, the first three being all of cubic symmetry, and the fourth of obviously hexagonal symmetry. They are shown, including the second variety of the dodecahedron, in the next screen picture (Fig. 4). He further considers that all four may be homogeneously deformed into analogous parallelohedra of lower orders of symmetry, without ceasing to fill space when closely packed. Hence, von Fedorow concludes that all crystal structures are of either cubic or hexagonal type, including not only truly cubic and hexagonal crystals, but their deformed derivatives. The cubo-octahedron (*e*, Fig. 4) is identical with Lord Kelvin's "tetrakaidekahedron," the most general parallel-faced cell (a hepta-parallelohedron) into which space can be regularly partitioned, and possessing the minimum surface for a given volume.

Unlike the atomic polyhedra of Pope and Barlow, these parallelohedra of von Fedorow are either molecular or polymolecular, in the latter event being made up of a small number of identically or symmetrically similar sub-polyhedra, termed by him "stereohedra," which represent the chemical molecules, just as already explained, when the grosser space-lattice unit is polymolecular, the stereohedra being arranged to build up the main parallelohedron (the space-lattice unit) on a definite plan, which may involve mirror-image juxtaposition. For example, a rhombohedral system of stereohedra is shown on the screen (Fig. 5), consisting of two kinds, R and L, one sort being the mirror-image of the other. Each rhombohedron representing the combined system is composed of six stereohedra, three of each kind, and a series of points, similarly situated one within each stereohedron R, would constitute a Sohncke point-system, while a "double-system" is obtained by adding a series similarly situated one within each stereohedron L. If a single point were taken to represent analogously each rhombohedral set of six stereohedra, we should have a rhombohedral space-lattice produced.

The valency theory of Barlow and Pope may or may not in the sequel prove to be correct, and some facts have recently been brought forward by Barker which tend to show that it will not hold in many cases of inorganic substances. Barker, who has had the good fortune to have worked in St. Petersburg with von Fedorow for more than a year, shows that, as the lecturer has always held, the true unit of volume is the molecular or atomic volume, as determined for the particular substance itself. The molecular volume is determinable by dividing the molecular weight of the substance by the specific gravity of its crystals at a definite comparable temperature, such as 20° C., but the determination of the atomic volume offers peculiar difficulty, and so far only comparative and indirect methods have been employed, chiefly by Sollas. By taking the volumes of the spherical units to be proportional to the atomic volumes (not those of the element in the free state, as enormous compression occurs on combination), and also determining the amount of free interstitial space by comparative methods of calculation, Sollas has achieved some remarkable explanations of the crystallographic characters of the two polymorphous forms of silver iodide and of the three forms of titanium dioxide, rutile, anatase, and brookite. We have as yet no guidance from von Fedorow as to the nature of the atomic units and the volumes which they occupy. It would not be surprising if the valency volumes of Barlow and Pope, in the cases of those elements for which their theory appears to work in a satisfactory manner, turn out to be identical with the atomic volumes as determined by the method of Sollas. As regards the compounds of carbon and hydrogen, Barlow and Pope have been most successful in accounting for crystallographic and chemical relationships, and it is at least significant that both Le Bas, from experimental work on the molecular volumes of liquid hydrocarbons, and Traube from an entirely different point of view, concur in assigning the relative volumes 4 and 1 to carbon and hydrogen atoms in combination respectively. If Traube's results for carbon and hydrogen be accepted, so must also those for the relative volumes of the atoms of the halogens, sulphur, oxygen, and nitrogen, his values being: F = 1; Cl, Br, and I = 7 each; S = 6; O = 2; and N = 3. As regards oxygen and nitrogen, he agrees with Barlow and Pope, but the latter take all the halogens as of unit valency volume, and sulphur as of valency volume 2. Barker shows that while in the binary sulphides, such as zinc sulphide ZnS, the sulphur is probably of volume

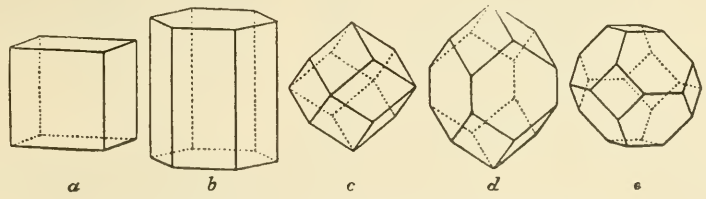

Fig. 4.—Fedorow's Types of Parallelohedra.

* A Discourse delivered at the Royal Institution of Great Britain, March 14, 1913.

2, in the sulphates, such as K_2SO_4 and $BaSO_4$, it is probably 6, as Traube insists; this conclusion is also in agreement with other work of Barker on some extraordinary cases of isomorphism, including that of barium sulphate with potassium perchlorate $KClO_4$, potassium permanganate $KMnO_4$, and the extraordinary compound potassium borofluoride KBF_4.

While it would thus appear that the atomic volume (in the substance itself, and including any interspace) is the

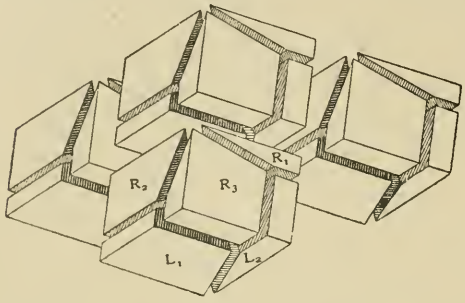

Fig. 5.—Fedorow's Stereohedra.

true effective volume concerned in crystal structure, and that it may be only a coincidence that, in the cases of a few prominent elements, it happens to be approximately proportional to the valencies of those elements (as certainly appears to be true in the cases of hydrogen and carbon, and possibly oxygen and nitrogen), there is a very considerable amount of the joint work of Barlow and Pope which is of permanent value. Their explanations of the preponderating cubic and hexagonal crystalline forms of the elements themselves, and of binary compounds such as ZnS, are doubtless correct, and it will be of great interest, in view of the next development to which attention must be called, to illustrate the case of zinc sulphide, and also the structure of that most interesting simple compound, silicon dioxide SiO_2, quartz, which has been worked out in a very complete manner by Barlow.

Barlow and Pope's idea of the structure of zinc blende, which merely assumes that the volumes of the atoms of

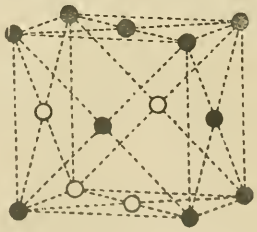

Fig. 6.—Space-lattice of Centred-face Cube.

zinc and sulphur are approximately equal, is that 16 molecules ZnS go to form the grosser unit of the crystal structure, the combined system or space lattice unit—that is, 16 atoms of zinc and 16 of sulphur. Only one zinc or one sulphur atom in every 16 is sameways orientated, and if we adopt von Groth's definition, we may give the structure of zinc blende as follows:—The crystals of zinc blende consist of two interpenetrating regular point-systems, one formed from zinc atoms, and the other from sulphur atoms; each of these two point-systems is built up from 16 interpenetrating space lattices, each of the latter being formed from zinc atoms or from sulphur atoms occupying parallel positions. All the 32 space-lattices of the combined system are geometrically identical.

Barlow and Pope have shown that the space-lattice in zinc blende is the third cubic one, in which a point is situated at each cube corner and also in the centre of each cube face. For this is the space-lattice corresponding to

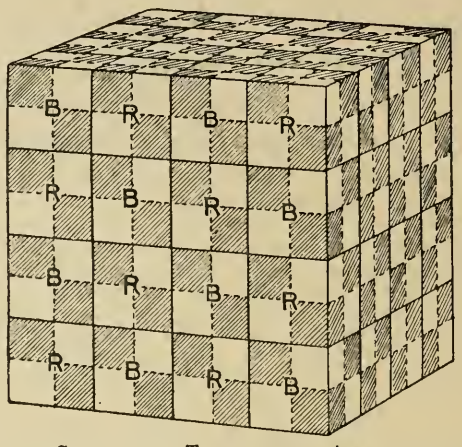

Fig. 7.—Scheme of Tetrahedral Arrangement of Zinc (B) and Sulphur (R) Atoms in Zinc Blende. (Unshaded Cubes unoccupied).

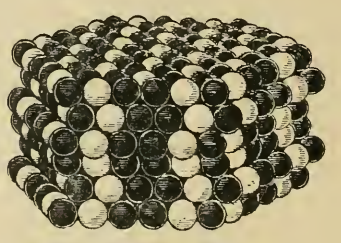

Fig. 8.—Barlow's Conception for Right-handed Quartz.

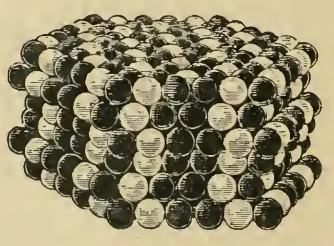

Fig. 9.—Barlow's Conception for Left-handed Quartz.

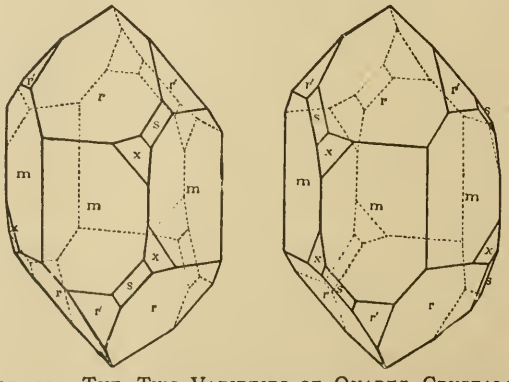

Fig. 10.—The Two Varieties of Quartz Crystals, Left-handed and Right-handed.

an assemblage of spheres of equal volume in closest packing. The space-lattice in question is shown on the screen (Fig. 6), and a pair of models of the arrangement are illustrated in the next two pictures, in the first of which the points are expanded into spheres of considerable size, and in the second they appear still further expanded into actual contact. The third stage, in which the expansion proceeds until all interstices are filled up and the spheres are converted into polyhedra, is left to the imagination. In the second picture the mutual arrangement of the spheres of the two elements in zinc blende, zinc and sulphur, is indicated by the yellow colouring of the sulphur spheres and the grey tinting of those of zinc. The tetrahedral mode of derivation of the structure, accounting for the observed hemihedrism, is also shown in another slide (Fig. 7). The eight larger cubes which together form the grosser unit are each supposed to be occupied by four smaller cubes of the same element, arranged tetrahedrally, and of zinc and of sulphur alternately in different larger cubes; on replacing the little cubes by spheres in contact the model represented in the second picture is produced.

Barlow's conception of quartz affords us an example in which the symmetry is trigonal, and of which there are two kinds possible, one of which is the mirror-image of the other, the two being helical in character and of the nature of right- and left-handed screws respectively. The two structures, as thus conceived, are represented in the next two slides (Figs. 8 and 9), the white spheres representing silicon atoms, and the black ones oxygen atoms, of which there are twice as many, corresponding to the formula SiO_2. The helical character is clearly shown, the white spheres being obviously arranged in a right-handed screw in one picture and a left-handed screw in the other. Right- and left-handed quartz crystals are so well known that it will not be necessary to do more than illustrate the fact by one or two experiments. First of all, two slides are shown (reproduced together in Fig. 10), one of a right-handed crystal and the other of a left-handed one, each exhibiting the characteristic little faces *s* and *x* of the right and left trigonal bi-pyramids and right and left trigonal trapezohedra, modifying the right and left corners formed by the meeting of the faces of the rhombohedron *r* and hexagonal prism *m*. That the right-handed crystal shows rotation of the plane of polarisation of light to the right, and the left-handed crystal optical rotation to the left, may be beautifully demonstrated by cutting a plate 1 mm. thick out of each crystal, perpendicularly to the axis, and using the device of 24 mica sectors, due to S. P. Thompson, which between crossed Nicols shows a black cross, the arms of which are deviated one sector to the right or left when the thin quartz plate is interposed, in accordance with the right- or left-handed nature of the plate. Also the phenomenon of the bi quartz, and of the natural bi-quartzes often produced by twinning of right and left individuals, may be illustrated, terminating with some beautiful cases of repeated twinning, including amethyst. The imitation of the phenomena of the two varieties of quartz, by crossing strips of mica in a right-handed or a left-handed pile, as shown by Reusch, may also be referred to and demonstrated, as affording some definite proof that the mineral does possess an analogous helical structure, complementarily opposite in its two varieties.

Now these two crystalline minerals, zinc blende and quartz, have been chosen advisedly as examples of crystal structure. For a remarkable series of experiments have recently been carried out by Laue, Friedrich, and Knipping at Munich, where the lecturer had the advantage of seeing some of the first photographic results last summer. In these experiments X-rays were passed through crystals of various substances, notably zinc blende, and, in more recent experiments by Laue at Zurich, quartz. The issuing rays were received on a photographic plate, on which they recorded a pattern of spots having the symmetry (full holohedral) of the space lattice present as the foundation of the crystal structure. These interesting photographs thus afford the first experimental and visible proof of the truth of the structure assigned to crystals by geometricians and crystallographers. By the great kindness of Professor Laue it is possible to exhibit the original photographs obtained with zinc blende, and one just obtained with quartz, the results for which Professor Laue has not yet published. Dr. Friedrich has also most kindly sent four excellent lantern slides expressly for this lecture.

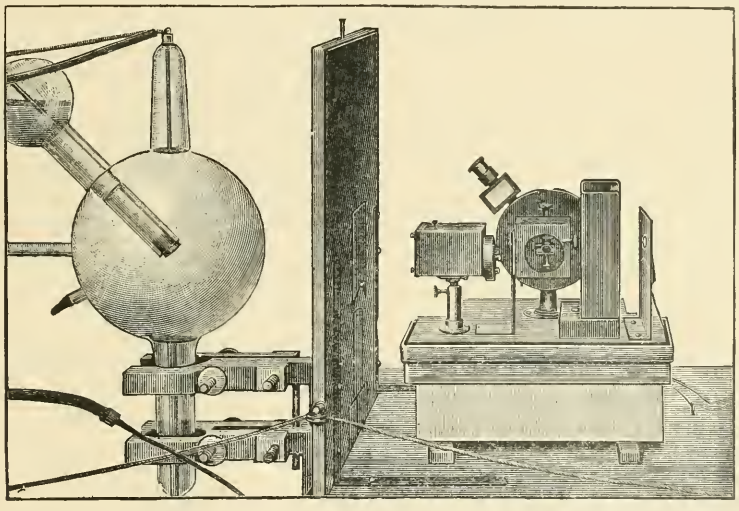

Fig. 11.—Apparatus of Friedrich, Knipping, and Laue for Passing X-rays through Crystals and Photographing the Effect.

In view of this further evidence of the richness of the original discovery by Sir William Crookes of the famous tube which is universally known by his name—producing under suitable circumstances of exhaustion the cathode rays when excited by the intermittent current from a Ruhmkorff coil, which rays, on their striking solid matter such as the soda glass walls of the tube, in turn give rise to the X-rays of Röntgen—it is fitting that some examples

of Crookes tubes should be exhibited in action, and Sir William Crookes has been so very kind as to arrange a display of some of his most beautiful productions, including tubes showing cathode rays impinging on a diamond and a ruby respectively, with glowing phosphorescence under the bombardment of the electronic corpuscles, in brilliant colours in each case. By the kindness of Messrs. Newton, it is also possible to exhibit in action two recent X-ray bulbs of the particular kind used by Laue and his colleagues.

Two pictures of the actual apparatus employed (one of which is reproduced in Fig. 11), most kindly also sent for the purpose of this lecture, and an explanatory diagram of it (Fig. 12), will enable the precise nature of the experiment to be grasped. A plate, 1 cm. square and 0·5 mm. thick, was cut from a good crystal of zinc blende parallel to a cube face, and adjusted on the crystal holder of a goniometer in the path of a very narrow pencil of X-rays from the bulb, isolated by their passage through a succession of lead screens (lead being impervious to X-rays) pierced by small holes. The last screen, which gave the final form to the pencil of rays, was a plate of lead 1 cm. thick, pierced by a cylindrical hole 0·75 mm. in diameter, and fitted with a delicate means of adjustment so that the axis of the boring could be brought exactly perpendicular to the

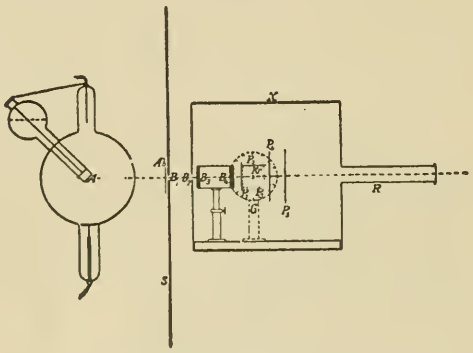

FIG. 12.—DIAGRAMMATIC REPRESENTATION OF APPARATUS OF FRIEDRICH, KNIPPING, AND LAUE.

A, Anticathode of X-ray Bulb; B_1, B_2, B_3, B_4, Diaphragms of Lead; K, Leaden Box-screen with Tubular Termination; S, Large Leaden Screen; G, Goniometer; P_1, P_2, P_3, P_4, P_5, Photographic Plates; Kr, Crystal; Al, Aluminium Plate.

crystal plate. The beam of pure X-rays of circular section, after passing normally through the crystal plate, was received on a Schleussner-Röntgen photographic plate, which was afterwards developed with rodinal.

The developed plate showed an intense circular spot at the centre, caused by the direct X-rays, and a considerable number of other spots of elliptical shape, arranged in a geometrical pattern. Three of these original photographs are exhibited on the screen. If a series of such photographic plates be used, at different distances from the crystal, the fact is revealed that the spots are formed by rectilinear pencils of rays spreading in all directions from the crystal, and some of them inclined over 45° to the direction of the incident rays. These deflected beams show similar properties to the original X-rays, ionising air and helium just like the latter, and with the same degree of variation with the pressure. Hence, there can be no doubt that the character of these deflected rays issuing from the crystal is that of unaltered X-rays, and that they are due to the reflection of X-rays by planes situated at different angular positions in the interior of the crystal. In short, we are in face of reflection of X-rays from planes of atoms in the crystal.

Now a study of the spots reveals the further interesting fact that the pattern shows the full symmetry (that of class 32) of the cubic system to which the crystal belongs, although zinc blende exhibits the slightly lower symmetry of the hexakis-tetrahedral class (31), one of the formerly so-called hemihedral classes of the cubic system. This clearly proves that it is the planes of similar and similarly situated (sameways orientated) atoms in the crystal that are producing the reflections, in other words, the planes of the space-lattice.

At first Laue, who published a separate memoir on the theory of the experiments, considered that it was the space-lattice due to similarly situated zinc atoms which afforded the spot-pattern, as he had been engaged with Prof. Summerfeld in experiments relating to the action of zinc on X-rays. But there appears no reason why the sulphur atoms should not be similarly capable of producing reflections of these extremely fine vibrations or corpuscles, and as the space-lattice is the same for both elements, according to all versions of the geometrical theory of crystal structure, there is really no reason why we should not consider the reflections as due to the general space-lattice of zinc blende. Laue considered the "molecules" of the crystal to form a three-dimensional grating—that is, a Raumgitter—and that each molecule is capable of emitting secondary vibrations when struck by incident electromagnetic waves from the X ray bulb; also that the molecules are arranged according to the simple cube space-lattice (No. 1). The incident waves being propagated parallel to one of the cube axes (edges), the wave-surfaces will be parallel to the plane of the other two cube edges. He then considers the spots to be interference maxima of the waves scattered by the orderly arrangement of the molecules in the crystal. The equations of condition were next found for interference maxima of direction cosines, α, β, γ, and for incident wave-length λ, and from the position of each spot the direction cosine of the pencil of rays which formed it was calculated, assuming all the transmitted pencils to come from the centre of the crystal. Thirteen spots in each quadrant were investigated, and in every case Laue's equations were satisfied; hence, the conclusion that the spots are due to interference of secondary Röntgen radiation appears to agree with the positions of the spots, provided only radiations of certain definite wave-lengths are present in the incident rays.

(To be continued).

MANUFACTURE AND USES OF CYANAMIDE.*

By E. J. PRANKE.

THE problem of the fixation of atmospheric nitrogen is one which has engaged the attention of scientists for the greater part of a century. The rapid growth of the fertiliser industry that has attended the development of agricultural science, and the great increase in the number and extent of chemical industries, during the past fifty years, has emphasised the necessity for artificial methods of maintaining and increasing the world's stock of combined nitrogen. One of the influences that stimulated immediate action was the introduction in 1887 by MacArthur and Forest, and at about the same time independently by Siemens and Halske, of Berlin, of the Cyanide Process for leaching gold and silver from their ores. This produced a strong demand for cyanides, which had hitherto been used to the extent of only a few hundred tons a year, principally in the dye industry and to a smaller extent in electroplating.

Attempts had been made early in the nineteenth century to bring about the direct synthesis of cyanogen from atmospheric nitrogen and carbon. Among other processes, that worked out in 1847 by Bunsen and Playfair, in which barium carbonate was heated in an atmosphere of pure nitrogen, seemed promising, but did not prove to

* Address before the Nashville Section of the American Chemical Society. From the *Chemical Engineer*, xvii., No. 3.

be commercially successful. The introduction of the electric furnace in 1894 by Moissan and by Willson, for the production of carbides on a large scale, gave new direction to the researches. Siemens and Halske, among others, adopted it for the working out of the problem of nitrogen fixation. In 1895 they worked on the process of Prof. H. Mehner, which consisted in fusing a mixture of sodium carbonate and carbon and conducting nitrogen through the hot mass. In the same year they took up the process of Prof. Adolph Frank and Dr. Nicodem Caro, which consisted in subjecting a mixture of barium carbide, sodium hydroxide, potassium hydroxide, and carbon at a high temperature to the action of steam and nitrogen. Frank and Caro, with the co-operation of F. Rothe, soon learned that dry nitrogen is essential to successful absorption. In 1898 it was found that barium carbide alone, heated to a temperature of 700 to 800° C., in an atmos phere of nitrogen, readily absorbs nitrogen and forms a product in which about 30 per cent of the nitrogen is present as barium cyanide and about 70 per cent as barium cyanamide. The reactions may be represented by the equations: $BaC_2 + N_2 = Ba(CN)_2$, $BaC_2 + N_2 = BaCN_2 + C$.

It was further found that on fusion of this mass with soda the cyanamide is converted to cyanide. This mass can then be leached with water, and the cyanide solution thus obtained can be converted to sodium ferrocyanide, which is easily separated in a pure form, and which can be sold as such or be converted into pure sodium cyanide by fusion with metallic sodium.

The interruption of the production of gold in Africa, due to the Boer war, caused a decline in the price of cyanide, which stimulated the search for cheaper methods of production. It was found that calcium carbide could not only be manufactured at a lower cost, but it had the advantage of a lower molecular weight. With calcium carbide a temperature of from 1100 to 1200° C. is required for absorption, but in this case the nitrogen is fixed exclusively in the form of calcium cyanamide. On fusion with alkaline salts the cyanamide is readily converted to cyanide, and this can be extracted and purified in the usual manner.

Agricultural experiments with the crude calcium cyanamide showed that this material is suitable for use as a nitrogenous fertiliser, and patents were issued in 1910 to Dr. Albert R. Frank, son of Prof. Adolph Frank, and to Herman Freudenberg, a co-worker of A. R. Frank, protecting the use of cyanamide for this purpose. The basic patent protecting the process of manufacture of cyanamide was issued to Prof. Dr. Adolph Frank and Dr. Nicodem Caro in 1908.

The large demands of agriculture for cheap nitrogenous fertiliser materials have directed the efforts of the manufacturers towards the production of cyanamide rather than of cyanides and other derivatives. At present the total output of sodium cyanide derived from cyanamide is only about 2000 tons per annum, while the world's production of cyanamide is estimated at about 120,000 tons per annum.

Manufacture of Cyanamide.

Calcium cyanamide is formed in accordance with the equation $CaC_2 + N_2 = CaCN_2 + C$. The raw materials, therefore, are calcium carbide and nitrogen. Calcium carbide is formed in accordance with the equation— $CaO + 3C = CaC_2 + CO$. The raw materials for this reaction, therefore, are lime and coke.

For the production of carbide, lime, from 1 inch to 2½ inches in size, and coke, about ½ inch, are mixed, in the proportions demanded by the equation, to produce a carbide about 80 per cent pure. The mixture is shovelled continuously into a 3-phase electric furnace. The furnace consists of a supporting base and four retaining brick walls which are filled with the lime and coke mixture, into which is submerged three carbon electrodes carrying the current. The resistance of the materials to the passage of the current raises them to a temperature at which the lime melts freely and combines with the coke to form liquid carbide. At intervals, as the carbide accumulates, it is tapped off through a suitable tapping hole at the side of the furnace into iron cars. After cooling, the carbide is crushed and ground to a fine powder, and is then packed in perforated cylindrical steel cans in the axis of which is a cylindrical paper core. The can with the carbide is set in a bricked walled oven, slightly larger than the can, and is covered with an iron lid. A carbon pencil is run through the paper core in the axis of the can. Upon passage of the electric current, the carbide is heated, nitrogen is admitted to the can, and the absorption takes place very readily, raising the temperature to about 1100° to 1200° C., at which point it is maintained until the absorption is complete. The reaction $CaC_2 + N_2 = CaCN_2 + C$ is exothermic, and the heat given out is almost sufficient to maintain the mass at the combining temperature. Upon completion of the reaction the cans are removed and the product is allowed to cool. It is a bluish black solid, containing small glistening crystals of pure calcium cyanamide.

Preparation.

The nitrogen required for the manufacture of cyanamide is separated from the air by either the liquid air process or the copper oxide process. The latter is in use at present by the American Cyanamide Company. The copper oxide process is based upon the ease with which heated copper combines with oxygen. The very finely divided copper suspended in a mass of asbestos or other inert material is contained in boiler shells provided with means for supplying heat externally. Air is pumped through the retort, which is at about 800° C., and is completely deprived of its oxygen. The nitrogen is then freed from carbon dioxide by passage through a caustic soda tower. The moisture is removed by refrigeration, followed by passage of the gas through layers of lime, and finally through calcium chloride. The nitrogen must be pure and dry, since otherwise there is a destruction in the nitrifying ovens of the carbon pencil and of calcium carbide in accordance with the following reactions:—

$$C + O = CO$$
$$C + H_2O = CO + H_2$$
$$CO + CaC_2 = CaO + 3C$$
$$CO_2 + 2CaC_2 = 2CaO + 5C$$
$$H_2O + CaC_2 = CaO + C_2H_2$$
$$3O + CaC_2 = CaO + 2CO$$

The oxidised copper in the nitrogen separation retorts is reduced in place by reducing gases, such as natural gas.

(To be continued).

Magadi Soda Company, Ltd.—We understand that this Company have already started to erect their works at the site recently acquired by them at Irlam, on the Manchester Ship Canal. Irlam lies seven miles west of Manchester, and the position of the works has been well selected, as it will be situated in the middle of what may be described as the largest soda consuming centre in Britain, if not in the world. The advantages of having the works so centrally situated are obvious where local consumption is concerned, and the export conditions from the Canal are no less advantageous. It is rumoured that the Magadi Soda Co. expect to secure a large share of the soda trade in the home market not only for pure soda ash, but also for various other soda products, such as caustic soda, bicarbonate of soda, and soda crystals, which will be manufactured at their Islam works. We hear that this new source of supply will be available some time in the course of next year, and the news will be interesting to all soda consumers, especially in view of the fact that the tendency of the latter nowadays is more and more to contract ahead for long periods.

THE SCIENTIFIC WEEK.

(From Our Paris Correspondent).

The Twenty-fifth Oceanographic Campaign.

The Prince of Monaco, at the Academy of Sciences, has summed up his last Oceanographic campaign. It was carried out in 1912, in the Northern Atlantic, towards the middle of that ocean at the west of the Azores. The Prince had with him Dr. Richard, the Director of the Museum of Monaco, Messrs. Banc and Gain, two distinguished naturalists, and a young learned Spaniard, M. Rafael Odon de Buen.

The Naval Captain Bourée, to whom we owe such remarkable apparatus for the study and capture of marine fauna, directed the researches in view of a diurnal vertical migration of a whole class of fauna, consisting of crustacea, fishes, and cephalopods. Veritable zoological treasures have been collected in fishings made at more than 5000 metres below the surface. Researches on the plankton were pursued at different depths, and M. Banc has studied the relation between the temperature of marine turtles and the quantity of sugar found in their blood. This campaign of the Prince of Monaco is his twenty-fifth expedition, and it constitutes, so to say, his Oceanographic silver wedding.

A New Organic Compound.

M. Daniel Berthelot, Professor of the Higher School of Pharmacy, and M. Gaudechon have just realised (by the direct union of carbonic acid and cyanogen, under the influence of ultra-violet rays) a new organic compound—an oxy-cyanuret of carbon, which is decomposed by hydrolysis with discharge of gaseous prussic acid. This experiment is somewhat dangerous, prussic acid being an extremely violent poison.

The Galvanoplastic Art of Electrotyping Nickel in Great Thicknesses.

The depositing of nickel in thick layers is a difficult problem to solve, on account of the tendency of this metal to rise up and peel off. The layer of nickel, in fact, exercises a considerable pressure on the conductor that it covers and tends to detach the metal already deposited. The cause of this exfoliation is probably the hydrogen that is discharged at the cathode at the same time as the nickel is deposited. In the presence of much hydrogen the metal forms a pulverulent deposit; if the gas is less abundant, the nickel is saturated with it, loses its suppleness, and peels off.

The operation is then a difficult one, and yet nickel in thick layers presents enormous advantages over other metals; amongst other things, in particular, it would permit of the manufacture of printing clichés that would be practically everlasting.

M. Hollard has tried to get rid of this noxious presence of hydrogen, by performing the electrolysis with a complex combination that gives out with difficulty its hydrogen to the current. He has employed fluoborate of nickel, which has given excellent results for an intensity of current of 1 ampère for electrodes of 14×18 centimetres at a distance of about 4 centimetres in a solution of about 1·08 of density. This bath deposits the nickel directly on cast-iron and on aluminium.

Spontaneous Generation.

The ideas of Professor Stephan Leduc, of the Faculty of Nantes, are well known. It is to him that we owe so many curious and original researches on the physico-clinical theories of life, electrical sleep, &c.

Professor Leduc has just published a new work in which he treats of the old idea, so much controverted, of spontaneous generation and of the researches undertaken by him to demonstrate that life is only a suite of physico-clinical phenomena.

Mystisism, finalism, nihilism, which, says Professor Leduc, always persist in biological sciences under diverse forms and in diverse degrees, do not explain the phenomenon of life.

The learned Nantois tries to explain this mysterious phenomenon by a succession of clinical or physical reactions. He has been able to reproduce, by means of salts and liquids, a whole series of osmotic productions; seaweed, ferns, worms, corals, and shells. The osmotic landscapes and the palæozoic forms obtained by Dr. Leduc are extremely curious. With sulphate of copper and sugar in a solution of ferro-cyanide of potassium he has obtained forms resembling the nerve-cells. With calcium and magnesia in an alkaline carbonate solution an imitation of marine seaweed was obtained.

In these seaweeds, cells, and infusoria, M. Leduc sees the images of life. It is the vital mechanism, the cellulary reproduction, the phenomena of karyokinesis which can be obtained expectatively in a laboratory crystalliser.

Biologists, however, think that Leduc's experiments are without interest. They do not see what relation can exist between the artificial curiosities of the physician of Nantes and living beings. Even if by improving his technic, M. Leduc manages to reproduce a worm or an ammonite more faithfully, how can that enlighten us on the origin and evolution of these beings? Such is not the opinion of M. Leduc. If, says he, we can manage, one day, to realise spontaneous generation, the study of form, the study of the multiplication of cells in a determined direction, according to the physico-clinical conditions described, my researches will be very useful. The experiments of M. Leduc are, nevertheless, in the present state of science very striking.

The *savant* has obtained productions which not only have the form of living beings, but which multiply, increase, feed, and present the phenomena of secretion and execretion, and even of sensibility like living beings.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, June 5th, 1913.

Sir Archibald Geikie, K.C.B., President, in the Chair.

The Croonian Lecture was delivered by Dr. Robert Broom on "*The Origin of Mammals.*"

An endeavour is made to trace the evolution of mammals from Cotylosaurian ancestors through the carnivorous Therapsida. In Upper Carboniferous times the line probably passed through some primitive generalised Pelycosaurs; in Lower Permian through primitive, probably Therocephalian, Therapsids. In Middle and Upper Permian the line passed through the Gorgonopsia. In Triassic times the mammalian ancestors were small generalised Cynodonts. In Lower Jurassic the mammals are so Cynodont-like, and the Cynodont so mammal-like, that in no single case are we absolutely certain which is which.

In the Therocephalia, the Gorgonopsia, and the Cynodontia, the skull is very mammal-like. The zygomatic arch is, as in mammals, formed by the jugal and the squamosal. The teeth are divided into incisors, canines, and molars. In the later Gorgonopsians there is an imperfect secondary palate; in Cynodonts a complete secondary palate as in mammals. In Permian Therapsids there is a single occipital condyle; in the Triassic Cynodonts there may be a single condyle slightly divided or two exoccipital condyles. There is, on passing from earlier to later types, a steady increase in the size of the dentary and decrease in the size of the other elements of the jaw. The quadrate also becomes much reduced in the higher

types. In Gorgonopsians and probably all earlier types the arch of the atlas is a pair of bones; in Cynodonts, as in mammals, there is a single arch.

It is argued that the small Gorgonopsians fed almost exclusively on the comparatively slow-moving, small, herbivorous Anomodonts. In the Trias the small Anomodonts became very rare, and the carnivorous Therapsids had to feed on other small forms, apparently the more active lizard-like Cotylosaurs, such as *Procolophon*. The change of habit resulted in the Cynodontia.

In Upper Triassic times the larger Cynodonts preyed upon the large Anomodont, *Kannemeyeria*, and carried on their existence so long as these Anomodonts survived, but died out with them about the end of the Trias or in Rhætic times. The small Cynodonts, having neither small Anomodonts nor small Cotylosaurs to feed on, were forced to hunt the very active long-limbed Thecodonts. The greatly increased activity brought about that series of changes which formed the mammals—the flexible skin with hair, the four-chambered heart and warm blood, the loose jaw with teeth for mastication, an increased development of tactile sensation and a great increase of cerebrum. Not improbably the attacks of the newly-evolved Cynodont or mammalian type brought about a corresponding evolution in the Pseudosuchian Thecodonts which ultimately resulted in the formation Dinosaurs and birds.

The following paper was read :—

"*Fossil Floras of the Wyre Forest, with Special Reference to the Geology of the Coalfield and its Relationships to the Neighbouring Coal Measure Areas.*" By E. A. Newell Arber, Sc.D.

CHEMICAL SOCIETY.

Extra Meeting, May 22nd, 1913.

Prof. William H. Perkin, LL.D., F.R.S., President, in the Chair.

The Van 't Hoff Memorial Lecture was delivered by Prof. James Walker, D.Sc., F.R.S.

A vote of thanks to Prof. Walker, proposed by Sir William Ramsay, K.C.B., F.R.S., and seconded by Sir William Tilden, F.R.S., was supported by Prof. H. E. Armstrong, F.R.S., and by Prof. F. G. Donnan, F.R.S., and carried with acclamation.

Ordinary Meeting, June 5th, 1913.

Prof. W. H. Perkin, LL.D., F.R.S., President, in the Chair.

Reference was made to the death, on May 16th, 1913, of Mr. Walter Shelley Spencer, of Farnworth, who was elected a Fellow on June 16th, 1887.

Messrs. P. P. Phillips and A. G. Dix were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Parmanand Mewaram Advani, M.A., B.Sc., Dayaram Jethmal Sind College, Karachi, India; Alan Hamilton Bateman, 12, Chadwick Road, Leytonstone, N.E.; Norman Phillips Campbell, B.A., Trinity College, Kandy, Ceylon; Mohamed Shams Eldin, B.Sc., The University, Manchester; Charles Huxtable, Devonia, Menlove Avenue, Liverpool; Benedict Hugh Rolfe, M.A., Wheatley, Oxon.; Philip Howard Stott, Tottington Road, Harwood, Bolton; John Algernon Lacy Sutcliffe, 44, Broad Street, Birmingham.

Messrs. H. Rogerson and E. Walker were elected Scrutators, and a ballot for the election of Honorary and Foreign Members was held. The following were subsequently declared duly elected :—Prof. Dmitri Petrovitsch Konovaloff (St. Petersburg); Prof. Alfred Werner (Zurich).

Of the following papers, those marked * were read :—

*157. "*Relation Between the Absorption Spectra and Constitution of Piperidine, Nicotine, Cocaine, Atropine, Hyoscyamine, and Hyoscine.*" By James Johnston Dobbie and John Jacob Fox.

The absorption spectra of piperine, nicotine, cocaine, atropine, and hyoscyamine have been examined, and it has been shown that the spectrum in each case is practically identical with that of the unreduced nucleus of the molecule, namely, piperic acid, pyridine, benzoic acid, and tropic acid (compare *Trans.*, 1911, xcix., 1254; 1912, ci., 77).

It has also been found that hyoscine (*l*-scopolamine), although differing in composition from atropine, gives the same spectrum, the difference between the two alkaloids lying only in the unreduced part of the molecule.

*158. "*Constituents of Hops.*" By Frederick Belding Power, Frank Tutin, and Harold Rogerson.

A consideration of the literature, together with the results of the present investigation, has led the authors to conclude that most of the products hitherto obtained from hops were of a very indefinite nature. A considerable number of well-defined substances, including some new compounds, have now been isolated and completely characterised.

It has been shown that the bitterness of hops is not due to any single substance, but is to be attributed to a number of products, which are mostly amorphous. Some of these products are soluble in water, whilst others represent constituents of the resin. One well-defined new crystalline substance, which possesses a bitter taste, has now been isolated from the resin, and designated *humulol*. This compound is phenolic in character, has the empirical formula $C_{17}H_{18}O_4$, and, when crystallised from 50 per cent acetic acid, forms needles of a pale fawn colour, which melt at 196°. Another new crystalline compound, of nearly the same percentage composition as humulol, but which has an orange-yellow colour and is devoid of bitterness, has been designated *xanthohumol*. This substance appears to possess the formula $C_{13}H_{14}O_3$, and melts at 172°.

The present investigation has furthermore shown that the resin of hops contains a large proportion of fatty acids and their esters, a fact which does not seem to have previously been observed or considered. It follows that such of the proposed methods for the valuation of hops as are based on the titration of extracts obtained by means of light petroleum and similar solvents are of very doubtful utility.

Discussion.

Mr. Grant Hooper congratulated Dr. Power and his co-workers on the interesting and valuable results of this long over-due investigation. He understood that the volatile essential oil which was removed by steam distillation of the extract upon which the authors worked was disregarded, but he asked whether they could say, nevertheless, if the whole of the odorous character of hops was connected with this volatile essential oil. He realised, of course, that the flavour of hops was of a compound nature, but he would like to know whether the authors were of opinion that the bitter character was exclusively associated with one or all of the resinous substances which had been isolated.

Mr. Chaston Chapman said that so far as he was aware no one had ever supposed that the separation of the resin constituents into the so-called α-, β-, and γ-resins represented a sharp chemical separation. It did, however, effect a certain degree of separation, and had done very good service from the technical point of view. He also thought that it had been very generally recognised for a considerable time that the bitter flavour of hops was due to a number of substances, and not to any one single constituent. The waxes and certain of the fatty acids were very general constituents of plants, and could not account for any of the characteristic properties of hops. In regard

to fatty acids, he was interested in finding that Dr. Power had met with nonoic acid, since some years ago he (Mr. Chapman) had called attention to the fact that this acid existed in the form of an ester in the essential oil, and was obtained by the oxidation of that oil with chromic acid. He suggested that in the hop itself that acid had probably resulted from the hydrolysis of the ester or from the oxidation of the oil. A number of chemists, who had made a special study of hops, both from the chemical and from the technological points of view, had described certain well-defined crystalline acids which were stated to be closely related to the true resins, and he (Mr. Chapman) did not see which of the constituents mentioned by Dr. Power corresponded with those so-called hop-bitter acids. It was evident that there was still a very great deal to be learned, and in the meantime it would be very interesting to know what light the work of Dr. Power and his colleagues threw on such a very important question as the preservative properties of hops, and how it explained the conversion (by simply boiling with water) of the petroleum-soluble and preservative constituents into products insoluble in petroleum, and possessed of little or no preservative properties. Unless the investigation helped to supply an answer to this and similar questions, its practical value would be considerably diminished. He would like to know from which constituent the valeric acid formed on oxidising the resin was derived.

Dr. POWER, in reply to a question by the President, stated that humulol and xanthohumol contained no nitrogen, and did not combine with acids.

In reply to Mr. Grant Hooper, it was stated that the aroma of hops could only be attributed to the essential oil. It was also explained that as the essential oil obtained in this investigation from an alcoholic extract of hops would naturally differ considerably in composition from a normal oil, as obtained by the direct distillation of hops with steam, it was not deemed desirable to record its characters.

With reference to Mr. Chapman's remarks respecting the character of the substances precipitated from a petroleum extract of the resin by alcohol, it was stated that, in view of the complexity of the extract, a product obtained by such a method would necessarily consist of a mixture of substances.

*159. "*Nitrogenous Constituents of Hops.*" (Preliminary Note). By ALFRED CHASTON CHAPMAN.

In 1910 the author published (*Proc. Intern. Congress of Brewing*, i., 93) the results of a preliminary investigation of the nitrogenous constituents of hops, and pointed out that he had commenced a detailed study of the various nitrogenous substances present, that he had already succeeded in obtaining certain crystalline bases, and that the work was being continued. As it had recently come to his knowledge that Power has been engaged in the investigation of this subject, it appears necessary to give some account of the work so far as it has gone. This work is being continued, and a further communication will be made to the Society in due course.

Owing to the presence in hops of large quantities of resinous materials, the isolation of the crystalline nitrogenous substances, which occur in relatively small proportions, is a matter of very considerable difficulty, and in the course of the investigation four different methods of obtaining these substances have been adopted. In some cases the hops themselves were extracted in the laboratory, but in other cases the extract prepared on the commercial scale was very kindly placed at the author's disposal by the Hop Extract Co., Ltd., to whom his thanks are due. Sometimes the extract represented hops of one particular kind, whilst at other times the extract from hops of mixed growths was intentionally used.

In the first method of working the concentrated aqueous extract of hops was precipitated with basic lead acetate, and the filtrate, after the removal of the excess of lead, was precipitated with phosphotungstic acid. The phosphotungstic precipitate was treated in the usual way, and to the solution containing the liberated bases, ammoniacal silver solution was added for the precipitation of purines. From this precipitate, *histidine* was obtained.

The filtrate from the purines, after having been freed from silver, was evaporated to dryness, and the residue submitted to a process of fractional crystallisation from absolute alcohol, followed by fractional precipitation with mercuric chloride. By these methods betaine and choline were isolated, and another base, which is being examined, was obtained.

From the filtrate from the phosphotungstic precipitate, *asparagine* was isolated, together with another amino-compound, which has not, at present, been identified.

In the second method the hops were mixed with lime, boiled with water, and the resulting mixture evaporated, dried, powdered, and extracted with alcohol. This extract was freed from alcohol, and precipitated with phosphotungstic acid. The solution of the bases thus obtained was precipitated with an ammoniacal solution of silver chloride, and from the resulting precipitate *adenine* and *hypoxanthine* were isolated.

In the filtrate from the purine precipitate, *betaine* and *choline* were again obtained.

In the third method the hops were extracted with ammoniacal amyl alcohol, which was in turn extracted with water acidified with hydrochloric acid. The acid extract was treated with phosphotungstic acid, and from the resulting solution of the bases *adenine* was again isolated. Betaine and choline were also again obtained.

In this extraction a small amount of a definitely alkaloidal substance was separated, but the quantity was insufficient for complete identification.

With the view of obtaining confirmatory evidence as to the nitrogenous constituents present, a concentrated aqueous extract of hops was treated with a mixture of alcohol and acetic acid, filtered, the filtrate freed from alcohol, and the residue extracted with water. This aqueous extract was then treated systematically with various immiscible solvents. The residue from the amyl alcohol extraction, on treatment with an alcoholic solution of oxalic acid, yielded a precipitate from which *hypoxanthine* was isolated.

From the aqueous extract, which is at present under investigation, a coloured nitrogenous substance was obtained, which is acid in character, and dissolves in alkalis, forming deep brownish red solutions. The examination of this substance is still in progress. That portion of the hop extract which was not dissolved by the alcohol-acetic acid mixture was repeatedly extracted with water, and the combined aqueous extracts treated with lead acetate and lead oxide. The filtrate, after having been freed from lead, was evaporated, and the residue, after fractionation with alcohol and the removal of the greater part of the potassium by means of tartaric acid, was precipitated by copper acetate with the addition of alcohol. From this precipitate, substances were obtained exhibiting properties which indicate that they are complex amino-acids or polypeptides, or more probably mixtures of these substances, and experiments are now in progress with the object of separating and identifying them.

Although not a nitrogenous compound, it may be mentioned that the insoluble residue from the alcohol-acetic acid extraction, when extracted with hot glacial acetic acid, yielded on cooling a crystalline substance, melting at about 70°, which was almost insoluble in alcohol and but sparingly so in acetic acid. This substance, which is the "wax" so frequently referred to in the literature of the subject, is being investigated.

From one of the alcohol extracts of the aqueous hop extract, well-formed crystals separated, which on examination proved to be potassium nitrate.

Results have been obtained showing the proportions in which the various groups of nitrogenous compounds are present in hops, and these will be given when the full communication is made. The author is also engaged in an investigation of the technological significance of thsee

nitrogenous constituents, the results of which will be published in due course.

*160. "*Anomalous Rotatory Dispersion.*" (Preliminary Note). By Thomas Martin Lowry and Thomas William Dickson.

By means of a photographic method the rotatory power of ethyl tartrate has been followed up to a point in the far violet region of the spectrum at which the ester produces a lævorotation comparable in magnitude with the maximum of dextrorotation observed with a yellow light. The rotations for 5 points observed photographically and for 13 wave-lengths observed with the eye can be expressed by the formula:—

$$\alpha = \frac{k_1}{\lambda^2 - \lambda_1^2} - \frac{k_2}{\lambda^2 \cdot \lambda_2^2}.$$

This confirms the view of Biot that anomalous rotatory dispersion is produced by the admixture of two substances differing in rotatory dispersive power as well as in the sign of their optical rotatory powers. Slow changes of rotatory power with time, comparable with those observed in methyl camphorcarboxylate, were found to take place in the liquid ester.

Discussion.

Dr. Lowry, in reply to a question by Mr. Walker, said that the effect of changing the temperature of ethyl tartrate or of altering the solvent would probably be to alter the magnitude of the two "rotation constants" without altering the corresponding "dispersion constants." It would be quite impossible, however, to detect small changes of dispersive power by analysing a curve which involved four arbitrary constants.

161. "*Equivalent Conductivities of Sodium Hyponitrite, Calcium Hyponitrite, and Hyponitrous Acid.* By Prafulla Chandra Ray, Rajendralal De, and Nilratan Dhar.

Equivalent conductivities of sodium hyponitrite, calcium hyponitrite, and hyponitrous acid at various dilutions have been determined at 0°. The ionic mobility of hyponitrosion is 38 (nearly) at 0°. Further, hyponitrous acid is found to be weaker than acetic acid and stronger than carbonic acid.

162. "*Double Carbonates of the Alkaline Earth Metals and Lead with Potassium Carbonate.*" By Rasik Lal Datta and Haridas Mukherjea.

In a paper on the double platinic and cupric iodides (Datta, *Trans.*, 1913, ciii., 426) it has been pointed out that the method of double decomposition in the presence of an excess of the substituted ammonium iodide was successful in the isolation of the double salts, and it was thought possible that such an indirect method might be useful in the formation of double carbonates which cannot be prepared by direct means. Recently Barre (*Comptes Rendus*, 1912, cliv., 279) tried to obtain some double carbonates by directly boiling the precipitated carbonates in saturated solutions of the alkali carbonates. In the case of calcium, he succeeded in preparing two salts only, namely, $CaCO_3,Na_2CO_3,2H_2O$ and $CaCO_3,K_2CO_3$, but he failed to obtain double salts with strontium carbonate and barium carbonate even after boiling them for twenty hours in a saturated solution of the alkali carbonates.

The method of preparation of these double salts consists in preparing a saturated solution of potassium carbonate at the room temperature and adding to it the solutions of the metals, preferably the chlorides, when the double salts are at once precipitated. In this case, as in that of the double cupric iodides, the precipitates are unstable in the presence of water, as they dissociate into their constituents, and hence could not be washed freely with water. It is for this reason that a saturated solution of potassium carbonate has been used throughout, and the precipitated salt separated from the mother-liquor by strong suction without washing with water.

Barium and strontium carbonates combine with only one molecule of potassium carbonate to form the salts $BaCO_3,K_2CO_3$ and $SrCO_3,K_2CO_3$ respectively. Lead carbonate, on the other hand, combines with 2 molecules of potassium carbonate to form the salt $PbCO_3,2K_2CO_3$, and calcium combines with 3 molecules of potassium carbonate to form the salt $CaCO_3,2K_2CO_3$. The abnormality of the composition of double lead and calcium carbonates might be explained in the case of the former as due to its heavy molecular weight, and in that of the latter as due to a special tendency for salt formation, since it forms double carbonates with potassium carbonate even by the direct method.

Potassium Barium Carbonate, $BaCO_3,K_2CO_3$ (compare Le Chatelier, *Comptes Rendus*, 1894, cxviii., 415).—To a saturated solution of potassium carbonate, a concentrated solution of barium chloride is added, when the double salt is at once precipitated. This is triturated in a mortar with the mother-liquor, and filtered with the aid of the pump. The salt could not be washed with water, since it decomposes into its constituents:—

0·1802 gave 0·1242 $BaSO_4$; Ba = 40·55.
0·7162 gave 0·4906 $BaSO_4$ and 0·3536 K_2SO_4; Ba = 40·27; K = 22·11.
$BaCO_3,K_2CO_3$ requires Ba = 40·89; K = 23·28 per cent.

Potassium Strontium Carbonate, $SrCO_3.K_2CO_3$.—When a concentrated solution of strontium chloride is added to a saturated solution of potassium carbonate, a transparent jelly-like mass is obtained, which gradually becomes opaque, and finally, on continued stirring, assumes a granular appearance. After triturating in a mortar, it was collected as usual with strong suction, and allowed to dry in the desiccator. The salt could not be washed by water, since it is decomposed by air:—

0·5393 gave 0·3287 $SrSO_4$; Sr = 29·07.
0·4365 gave 0·2704 $SrSO_4$; Sr = 29·55.
$SrCO_3,K_2CO_3$ requires Sr = 30·52 per cent.

Potassium Calcium Carbonate, $CaCO_3,3K_2CO_3$ (compare Le Chatelier, *loc. cit.*; Bütschli, *Verb. Naturhist.-med. Ver. Heidelberg*, [2], viii., 277).—This is obtained similarly to the above salt, at first as a transparent jelly, which gradually becomes opaque, and is finally transformed into a fine crystalline powder, which could be collected very easily. The salt was tested for water of crystallisation, which, however, could not be found.

1·0882 gave 0·176 CaO; Ca = 7·73.
0·4726 gave 0·0544 CaO; Ca = 7·85.
$CaCO_3.3K_2CO_3$ requires Ca = 7·77 per cent.

Potassium Lead Carbonate, $PbCO_3,2K_2CO_3$.—This is obtained as an amorphous precipitate by adding a concentrated solution of lead acetate to a saturated solution of potassium carbonate. After triturating in a mortar, it was collected by the aid of the pump, when it remained on the filter as a sticky mass, which was allowed to dry in the desiccator. The salt could not be washed for reasons previously assigned.

0·9268 gave 0·5174 $PbSO_4$; Pb = 38·19.
0·5462 gave 0·3018 $PbSO_4$; Pb = 37·73.
$PbCO_3,2K_2CO_3$ requires Pb = 38·23 per cent.

The authors are at present engaged in preparing other double carbonates of the series, not only with potassium carbonate, but also with the carbonates of the substituted ammonium bases.

(To be continued).

SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS.

Ordinary Meeting, June 4th, 1913.

Mr. Leonard Archbutt, President, in the Chair.

Mr. Frank Sturdy Sinnatt was elected a Member of the Society.

Certificates were read for the first time in favour of Messrs. John Joseph Eastick, 2, St. Dunstan's Hill, London, E.C., and J. F. Millar, Cawnpore, India.

Certificates were read for the second time in favour of Messrs. Charles William Birch, Ulick Richardson Evans, and Harold Warren Hill.

The following papers were read and discussed :—

"*An Electrochemical Indicator for Oxidisers.*" By ERIC K. RIDEAL and ULICK R. EVANS.

A need has long been felt for an easy means of detecting and estimating small traces of oxidising sterilisers (such as chlorine, hypochlorites, ozone, &c.) remaining in waters which have been treated with such substances.

An apparatus designed to meet this want consists of a platinum rod enclosed in a copper tube through which the liquid to be tested passes. The copper and platinum are joined to the poles of a sensitive current measurer, and if the water contains a powerful oxidiser, the current produced by virtue of the depolarising action of such an oxidiser is indicated on the scale, which can be graduated to read directly in parts of free chlorine, for instance, per ten million.

The method does *not* depend on the measurement of the conductivity of the liquid.

"*The Estimation of Tannin in Tea.*" By HENRY L. SMITH.

The tannin of tea may be determined by the method devised by A. C. Chapman (*Journ. Inst. Brew.*, 1907, vol. xiii., and vol. xv., 1909) for the determination of tannin of hops.

The caffeine must first be removed from the tea infusion by extraction with chloroform, or some will be carried down with the precipitate. The tannin is precipitated by the addition of a saturated solution of cinchonine sulphate and the cinchonine tannate filtered off, dried, and weighed.

The precipitate contains 45 per cent of cinchonine and 55 per cent of tannin. Concordant results can be obtained if the conditions are adhered to.

"*The Detection and Estimation of Nickel by means of α-Benzildioxime.*" By FREDERICK WILLIAM ATACK.

A new reagent for nickel is proposed, viz., an ammoniacal alcoholic solution of α-benzildioxime. The reagent is quite as delicate as the dimethylglyoxime reagent of Tschugaeff, and has the advantage that the coloration is produced almost immediately even with minute traces of nickel, whereas with dimethylglyoxime the solution has often to be allowed to stand for a considerable time.

α-Benzildioxime is particularly suitable for the estimation of small amounts of nickel, giving a much more insoluble precipitate which contains only 10·93 per cent of nickel, whereas that from dimethylglyoxime contains 21·31 per cent of nickel. Moreover, quantitative precipitation takes place immediately with the new reagent, whereas the precipitation is only complete after some time in case dimethylglyoxime is used. The method is available in presence of cobalt, iron, manganese, zinc, chromium, and magnesium.

"*Analysis of various East Indian Tanned Hides.*" By M. C. LAMB.

The analyses of about sixty samples, obtained from reliable sources, of various tannages of East Indian hides have been made with the object of ascertaining which particular tannages are most liable to adulteration by the addition of mineral matter and oil. The results of the various analyses are given in detail and show that the amount of adulteration suspected in these imported tanned hides is not nearly so prevalent as is generally anticipated and understood by the trade.

"*Sterilisation of Rag Flock Samples.*" By LESTER REED.

It is found by experiments on flannel containing ammonium chloride, that only a very small loss of chloride occurs on heating either in closed or open jars to 140° C. for five hours in a paraffin oven.

"*General Method for the Detection of Caramel.*" By P. F. THOMPSON.

The author deals with the general chemistry of caramel, and recommends α-naphthol, or better still resorcinol, as the best reagent for the detection of caramel in organic liquids such as vinegar, spirits, and flavouring essences.

PHYSICAL SOCIETY.

Ordinary Meeting, May 30th, 1913.

Prof. A. SCHUSTER, F.R.S., President, in the Chair.

PROF. A. W. BICKERTON, A.R.S.M., gave the Society an account of his theory of "*The Origin of New Stars.*"

The energy developed by mutual fall of colliding suns is so great that shearing must ensue. Hence the problem of oblique impact of all suns has to be taken in two divisions. First, the actually colliding parts that are torn away and coalesce; and, secondly, the parts that escape the collision but are profoundly influenced by it. The impact of meteoric swarms, nebulæ, and siderial systems must similarly be taken in two parts. The coalesced part is called the third body. The properties of this new body are best studied in the third star resulting from grazing suns.

The third star is thermodynamically unstable, and selectively sorts its atoms into ensphering shells. It rotates, and has at its formation a special distribution of its elements.

It must produce a new star. Its deduced properties correspond in every detail with the three criteria of thermodynamic intensity, complex light curve, and all the physical peculiarities shown in each series of the spectrograms of novæ.

The deduced properties of the third body satisfy all three, not merely generally, but in the minutest detail, and no characteristic of novæ has been observed that is in opposition to this explanation. The molecular velocity developed by the complete collision of stars is much less than the critical, hence the coalesced body is a permanent star. In the case of a third body the gravitating power is so small that the molecular velocity is above the critical.

Novæ have a mean maximum intensity of about 3000 times that of the sun, and their mean mass is probably less than the sun. The deduced mean molecular velocity of the newly formed third body is about 200 miles a second. The atoms as they attain the same temperature change their velocity and tend to have a kinetol or energy of unit mass the inverse of their atomic weight. Hence the body tends to divide into ensphering shells of light gas, chiefly hydrogen and a nucleus of heavy elements. The nucleus expands and passes its volume of equilibrium. It then shrinks again, and once more passes its volume of equilibrium, becoming too small; then it expands again and so continues to oscillate. Hence the deduced light curve of the third body has a sudden rise, then an upward curve to maximum, followed by a fall, and it finishes with a gradually diminishing oscillatory curve. The observed curve is identical with these deductions.

The deduced spectrograms change in character. At first they should be stellar; then, as the hydrogen forms ensphering shells, blaze bands should form. These should be of considerable width, because the gas shell is expanding quickly in every direction. Immediately in front of the nucleus, the gas coming towards us produces isochromatic reversion, and fringes the short wave edge of the blaze bands with shadow bands. As the ensphering shells of hydrogen get larger and less dense, this power of reversion dies out. In the spectra of every fully observed nova all of these changes have been seen.

The PRESIDENT remarked that Prof. Bickerton's theory gave a satisfactory explanation of many of the phenomena of new stars. There were some points on which further information was required. One point in particular was the

enormous velocities often obtained both in new stars and in solar prominences when these were calculated according to Doppler's principle. It was well known that there was a definite limit to the velocity which could be produced by a gaseous explosion. Even when a compressed gas expanded into a vacuum the velocity acquired could not be greater than the mean molecular velocity no matter how great the pressure. As this was generally many times less than the observed velocities it seemed to indicate the presence of other forces at work, such as electrical ones.

Dr. W. G. Duffield stated that he had been considering the spectra of new stars in relation to the pressure effect. The bright blaze lines seemed due to pressure, as both in them and in the pressure effect the displacement was proportional to the cube of the wave-length, while the dark lines showed a displacement simply proportional to the wave-length and the same for all elements which indicated a Doppler effect.

Prof. A. W. Bickerton, in reply, stated that his inspection of Prof. H. F. Newall's photographs of Nova Geminorum showed there were great differences in the velocities for different elements. The iron lines showed a much less velocity than the hydrogen ones.

A paper on "*Electro-thermal Phenomena at the Contact of Two Conductors with a Theory of a Class of Radio-Telegraph Detectors*," was read by Dr. W. H. Eccles.

The paper is a purely theoretical one, and deduces mathematically the laws connecting the current and the applied E.M.F. in a circuit containing a light contact of two conductors. When an electric current passes across a light contact of two different substances, heat is liberated or absorbed in accordance with the law of Peltier, heat is generated in accordance with the law of Joule, and, in the regions of the conductors where there is a temperature gradient, heat is liberated or absorbed in accordance with the laws of the Thomson effect. These thermal actions are very noticeable in contacts made of badly conducting natural oxides or sulphides on account of the high resistivity and the large thermoelectric effects in these substances. The low thermal conductivities of these substances exalt the electrical consequences by conserving the heat. The bulk of the wireless telegraphy of the world is carried on by such contacts as these, and the present paper therefore constitutes a theory of the action of these detectors.

The general equation connecting the current across a contact and the P.D. between two points of the circuit is deduced, and is found to be of fourth degree when the difference of the specific heats of electricity in the conductors is not zero. The curves are discussed and plotted for all the principal variations of value of the Thomson effects, the Peltier effects, and the resistivity-temperature coefficients of the substances. It is shown that, in general, when a contact is used as a radiotelegraph detector, there may be some coherer action mixed up with the thermoelectric "rectifying" action, and that, whether there is or is not any coherer action, the principal features of the characteristic curve connecting current and E.M.F. are determined by the Thomson rather than by the Peltier effect. Thus, if two contacts could be made having all their electrical and thermal properties of equal measure excepting the Thomson property, of which the measures were of opposite signs, the curve connecting current and E.M.F. for one contact would rise more rapidly on, say, the side of positive E.M.F, than on the side of negative E.M.F., and vice versa for the other contact, and this although a direct experiment of applying heat to the contacts in turn and observing the consequent thermoelectric forces showed these to have the same direction in both.

Dr. A. Russell considered Dr. Eccles's fundamental equation very valuable. He thought Dr. Eccles's definition of the efficiency of a detector useful and the method of arriving at it very neat, but he did not think the curve of efficiency given by Dr. Eccles would be much use. What was wanted to tell a good detector was the shape of the function showing the relation between the current and the E.M.F.

Prof. C. H. Lees thought it was important to have shown that the well-known phenomena of thermoelectricity and variation of resistance could explain the behaviour of contacts. The theory was quite elastic enough to explain more complicated characteristic curves than those now considered, as the resistance was not strictly a linear function of the temperature and the heat conductivity also was not a constant.

Mr. P. R. Coursey stated that Dr. Fleming considered that rectification was due to flexures in the characteristic curve, and experimental results agreed with this view.

Dr. J. A. Fleming communicated the following:— With reference to Dr. Eccles's remarks on the characteristic curves of certain rectifying detectors, I believe I was the first to point out, in a British patent specification, No. 13,518 of 1908, the conditions under which certain rectifiers of oscillations, such as my glow-lamp detector, can be operated with an added E.M.F. as a more sensitive detector than by use as a mere rectifier without such E.M.F. Long before that date a large number of measurements of characteristic curves of my valves and other detectors had shown that there were sudden changes of curvature in them. The method of detecting these was to plot a first and second differential curve from the volt ampere characteristic. In the above specification I described simple means of applying the boosting voltage in the case of a glow-lamp detector by using a potentiometer wire in connection with the same battery which incandesces the glow-lamp. With certain detectors this is a more sensitive arrangement for detecting oscillations, but it is unfortunately as yet impossible to construct glow-lamp detectors or oscillation valves with predetermined characteristics. I have, however, one glow-lamp detector which when worked in this manner is more sensitive than any electric wave detector I have ever met. We have not yet found the way to reproduce it. I referred to these experiments in a Friday evening discourse at the Royal Institution, and exhibited a diagram showing the characteristic curve of a certain valve and its first and second differential curves. The scheme of the circuits and the method of working is fully explained with diagrams on p. 481 of Chapter VI. of the second edition of my book on "The Principles of Electric Wave-Telegraphy and Telephony." Since that date a very large amount of information has been collected in my laboratory on the form of the characteristic curves of a number of contact and crystal detectors. Mr. Coursey made for me a very extensive collection of such measurements about eight or nine months ago, but this information and a numerous set of curves depicting the observations has never yet been published. The results do not, however, fall in with any very simple theory of such rectifying detectors. The point to be explained is the reason for this sudden change in curvature in the characteristic. It is obvious that if there is such a change of curvature then the mean value of the current through the detector and, therefore, in a telephone, in series with it, will be increased if we add to the alternating E.M.F. acting on the detector a steady unidirectional E.M.F. of value exactly corresponding to the abscissa of the characteristic at that point of change of curvature.

The Author, in reply to Prof. Lees, stated that all the coefficients of his fundamental equation were variable with temperature. In reply to Prof. Fleming, he stated that the paper fully explains the main changes of curvature in the characteristic of a crystal detector, but does not touch on the theory of the vacuum valve.

A paper on "*The Extraordinary Ray resulting from the Internal Reflection of an Extraordinary Ray at the Surface of an Uniaxal Crystal*," by Mr. James Walker, was taken as read.

By the principle of least time it is shown that the diameter of the extraordinary wave-surface described round the point of incidence, that is, conjugate to the reflecting sur-

face, is coplanar with the incident and reflected extraordinary rays and is the median of the triangle formed by these rays and a parallel to the reflecting surface.

The direction-cosines of the reflected ray are then obtained in terms of those of the incident ray and the said diameter of the wave-surface.

A paper "*On the Evaluation of Certain Combinations of the Ber, Bei, and Allied Functions*," by Mr. S. BUTTERWORTH, was taken as read.

CORRESPONDENCE.

TREATMENT OF DISEASE BY DRUGS.

To the Editor of the Chemical News.

SIR,—The sections "Pharmaceutical Chemistry" and "Chemotherapy" in Mr. Carl Duisberg's article (CHEMICAL NEWS, cvii., pp. 246-7) would seem to call for comment, and more so as the writer is himself claiming credit for work done.

Now that our foremost doctors are discarding drug treatment, and relying on diet (and fasting), fresh air, water treatment, applied both internally and externally, and rest, it would seem to be a sad waste of time to devise new mercury or other poisonous compounds and place them on the market by the "latest" commercial methods, the details of which would make interesting reading for the subjects so experimented upon.

Surely it is now recognised that it is but little use to "combat the *symptoms* of disease," as Mr. Duisberg has it, and also that a fever being nature's method of relieving an over-charged system should be allowed to run its course with neither food nor drugs to hinder.

A slight acquaintance with nature-cure methods as practised extensively in Germany and to an extent—happily increasing—in this country, should liberate a number of skilled chemists from the pursuit of a phantasy, and save many animals from painful lives and deaths at their hands.

It may interest some of your readers to know that even syphilis and leprosy *have been cured without drugs*, and that all disease is treated as one.—I am, &c.,

VOX HUMANA.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Academie des Sciences. Vol. clvi., No. 12, March 25, 1913.

Electrical Conductivity of Tellurium.—Paule Collet.—The resistance of tellurium varies very irregularly with the pressure provided that the latter is lower than about 30 to 40 grms. per sq. mm. Above this value the resistance first remains constant for a given potential difference, and afterwards an increase of pressure produces a diminution of resistance. After the passage of an exciting current tellurium exhibits a residual electro-motive force for about a minute. For durations exceeding several seconds the resistance is a function of the time during which the current passes, but if the duration is of the order of a fraction of a second the resistance is definite and independent of the time.

Bulletin de la Société Chimique de France. Vol. xiii.-xiv., No. 7, 1913.

Preparation of α-β-diketonic Ethers.—A. Wahl and N. Doll.—The α-β diketonic ethers can be prepared by treating a solution of the β ketonic ether in a mixture of anhydrous ethyl oxide and acetic anhydride with nitrous vapours, and extracting the ether produced by fractional distillation. The α-β-diketonic ethers are highly coloured orange liquids which combine with water and alcohol with the liberation of much heat. The alcoholates do not crystallise while the hydrates of the cyclic compounds are crystalline. The diketones distil in vacuo without decomposition, and their boiling-points are practically the same as those of the β-ketonic ethers from which they are derived. They are energetic reducing agents.

Monoiodohydrine of Glycol derived from Cinnamylmethyl Ether.—Henri Beaufour.—The author has already prepared a glycol iodohydrine of the methyl ether of cinnamic alcohol, and has now proved that its formula is $C_6H_5.CHOH.CHI.CH_2.OCH_3$. It reacts with dry potash to give the corresponding oxide, and gives an amino-alcohol with dimethylamine in benzene solution. Alkyl iodohydrines such as $C_6H_5.CH(OCH_3).CHI.CH_2.OCH_3$ can be prepared similarly, and are much more stable than the monoiodohydrine.

Monohydrated Ferrous Sulphate.—Daniel Florentin.—Ferrous sulphate containing one molecule of water is a perfectly stable salt which is not hygroscopic and is not oxidisable in ordinary conditions. It may be obtained very easily by dehydrating the salt containing 7 molecules of water with 50 per cent H_2SO_4. Owing to the constancy of its composition, the ease with which it is obtained, and its convenience in use, it may be regarded as a salt which can be employed for the determination of the strength of MnO_4K solutions.

Atti della Reale Accademia dei Lincei. Vol. xxii. [i.], No. 4, 1913.

Notes on the Azoxy Compounds.—Angelo Angeli.—The oxidation of azo-derivatives by means of hydrogen peroxide gives azoxy compounds quantitatively according to the equation—

$$C_6H_5.N=N.C_6H_5+H_2O_2=C_6H_5.(N_2O).C_6H_5+H_2O.$$

The symmetrical azo derivatives all furnish a single type of azoxy compound when oxidised thus. Two different azoxy compounds correspond to the asymmetrical azo-derivatives, and these two compounds differ from one another in the position of the oxygen atom. Thus the α-form may be represented by the formula $C_6H_5.N=N.C_6H_4Br$ (with O), and the β-form by $C_6H_5.N=N.C_6H_4Br$ (with O).

Effect of some Organic Acids on Decomposition of Hydrogen Peroxide.—C. Porlezza and G. Norzi.—Manganese sulphate in neutral solution has a decided catalytic action in the decomposition of hydrogen peroxide. The rate of decomposition is appreciably lowered by the presence of uric acid, and to a slighter extent by oxalic, hippuric, and benzoic acids.

MEETINGS FOR THE WEEK.

THURSDAY, 26th.—Royal Society. "Light Sensations and the Theory of Forced Vibrations," by G. J. Burch. "The Fluctuation in the Ionisation due to γ-Rays," by P. W. Burbidge. "Force exerted on a Magnetic Particle by a varying Electric Field," by J. G. Leathem. "Luminosity Curve of a Colour-blind Observer," by W. Watson. "Critical Study of Spectral Series—Part III., The Atomic Weight Term and its Import in the Constitution of Spectra," by W. M. Hicks. "Band Spectrum attributed to Carbon Monosulphide," by L. C. Martin. "Phosphorescence of Mercury Vapour after removal of the Exciting Light," by F. S. Phillips.

THE CHEMICAL NEWS.

Vol. CVII., No. 2796.

GREAT ADVANCE IN CRYSTALLOGRAPHY.*

By A. E. H. TUTTON, D.Sc., M.A., F.R.S.

(Concluded from p. 292).

The lecturer pointed out, in an article in *Nature*, of November 14th, 1912, that the structure of zinc blende was probably not so simple as had been assumed by Laue, and that the space-lattice with a point at the centre of each side of the cube (No. 3) was the more probable one, the structure being that assigned to it by Barlow and Pope, as already described in this lecture.

A satisfactory explanation has since been advanced by W. L. Bragg, which does accord with this structure and with other essential conditions referred to by the lecturer, which altogether avoids the assumption of only a few wave-lengths, and which agrees with a simple reflection of unchanged X-rays from the planes of points of the general space-lattice of zinc blende. He regards the incident radiation as composed of a series of independent pulses, which, falling on a number of atoms definitely scattered in a plane, are separately reflected, each atom acting as a centre of a secondary wave, and the whole building up a wave-front. The interference maximum is thus due to the reflection of the incident pulses from a system of parallel planes of similar atoms, that is, from one of the parallel series of planes of the space-lattice. Now besides the principal planes of the space-lattice, the cube planes, the points of the space-lattice also lie in a considerable number of other planes, all of which are possible crystal faces corresponding to rational indices. For instance, the octahedral planes are very easily traced, as also those of the rhombic dodecahedron. A minute fraction of the energy of a pulse traversing the crystal will be reflected from each parallel plane in succession, and the corresponding interference maximum will be produced by a train of reflected pulses. The crystal thus actually manufactures rays of definite wave-lengths, just as a diffraction grating does, the only difference being here in the extremely short length of the waves, which is the very reason why X-rays can penetrate in this manner into the Raumgitter structure. Each incident pulse produces a train of pulses, resolvable into a series of wave-lengths, λ, $\lambda/2$, $\lambda/3$, $\lambda/4$, &c., where $\lambda = 2\,d \cos\theta$, d being the shortest distance between successive identical parallel planes in the crystal, and θ the angle of incidence of the primary X-rays on the plane of points of the space-lattice. The intensity of any spot depends on the energy in the spectrum of the incident radiation characteristic of the corresponding wave-length, and this varies considerably so that certain parts of the spectrum are much more pronounced than others. Also it depends on the number of reflecting atoms in the plane, that is, on the reticular density of the possible crystal face corresponding to the plane. Hence, the greater the reticular density, the more intense the spot produced in the photograph. As reticular density is also proportional to importance of face, the primary faces having the greatest reticular density, it follows that the most important facial planes reflect the intensest spots, a fact which may prove of great value in enabling us to discover the real primary planes in doubtful cases. Each spot reflected by a plane (considered as passing through the origin and two other points) lies at the intersection of two ellipses, and the figure on the screen (reproduced in Fig. 13), showing an analysis of one of the spot photographs, exhibits this clearly. Indeed, the plane of atoms corresponding to any spot can be found from the two ellipses; for each ellipse is the section of a cone by the plane of the photographic plate, the axis of the cone being the line joining the origin (centre of the triaxial system, and considered as one of the three points determining the plane) and the particular atom (the second or third point of the three, of definite co-ordinates), and the generator of the cone being the incident beam.

The interesting results of Bragg are in full accord with the assumption of the centred-face cubic space-lattice

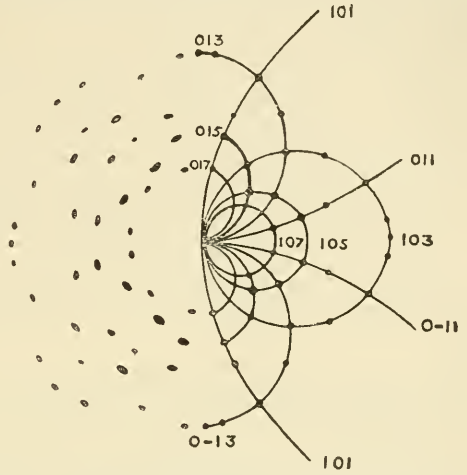

Fig. 13.—Analysis of Spot-photograph of Zinc Blende.

(No. 3), but not with either the simple-cube or the centred-cube space-lattice (Nos. 1 and 2). They also account for the elliptical shape of the spots. The amount of ellipticity depends on the distance of the photographic plate from the crystal. When the two are very close the spots are round, but they become more and more elliptical as the plate is receded. The phenomenon is due to the fact that the initial rays are not strictly parallel, and the effect will be clear from the next slide (Fig. 14). The vertically diverging

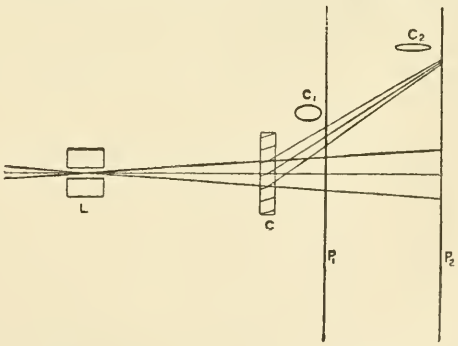

Fig. 14.—Explanation of Elliptical Shape of Spots.

rays striking the reflecting planes of the upper part of the crystal meet them at a less angle of incidence than those of the lower part, and so the reflected rays converge. Horizontally diverging rays, however, diverge still more on reflection. Hence the section of the reflected beam is an ellipse with major axis horizontal.

It is of importance to note that the centred-face cubic space-lattice is characteristic both of the arrangement of identically (sameways) orientated and environed atoms of the same element, zinc or sulphur, and of the atoms of both elements regarded as equal spheres in contact. In

* A Discourse delivered at the Royal Institution of Great Britain, March 14, 1913.

the slide already shown of Barlow and Pope's model, the spheres of sulphur are coloured yellow to distinguish them from the grey-coloured spheres of zinc. If we ignore the colour and consider them as similar spheres, we see that they form the centred-face cubic arrangement. The hemihedral nature of zinc blende is, however, very likely connected with some real difference of volume between the atomic spheres.* As the spot figure is holohedral it would appear to be due to the space-lattices of similarly placed atoms of either (but in each lattice only one) element, rather than to the spheres of the combined system of atoms.

This latter conclusion is further borne out by the result of the new work by Laue on quartz. The photograph now shown, so kindly sent by Prof. Laue, exhibits the trigonal nature of the symmetry very clearly, and Prof. Laue informs me that the same figure is afforded by both right and left quartz, so that it does not reveal the hemihedral character of quartz which has been demonstrated this evening, but possesses the full holohedral symmetry of the trigonal space-lattice, and exhibits the threefold nature of the axis of symmetry which is perpendicular to the plate and along which the X rays were directed.

Prof. Laue has also experimented with the crystals of a number of other cubic substances, and, like zinc blende, they all show holohedral symmetry about a tetragonal axis.

W. L. Bragg has found that stronger photographs of the same nature can be obtained from mica, using nearly grazing incidence, and it is by use of this fact that Mosely and Darwin have been able to study the reflected rays electrically, and found them to resemble ordinary X-rays.

By the kindness of Mr. Bragg, a diagram of his apparatus and a positive lantern slide of one of his mica spot photographs are exhibited on the screen. The large white spot is due to the direct rays; the next brightest but smaller spot considerably above the direct one is due to rays reflected from the cleavage plane, and the other spots to reflections from other possible faces and planes of the monoclinic space-lattice; all the spots are such as are compatible with this lattice, and with the well known fact that the monoclinic angle is almost 90°. The spots lie on two ellipses intersecting at the central direct spot and at the upper bright one, each ellipse corresponding to a set of parallel rows of points, the crossing of the two sets forming rhombic parallelograms, the basal edges of the monoclinic prismatic space-lattice cell of mica.

Incidentally these experiments appear likely to throw light on the much-debated question of the nature of the X-rays. As all the experiments unite in indicating that a fraction of the X-rays suffer reflection at the planes of atoms parallel to the more important possible crystal faces, all being planes of atomic points of the space-lattice, it would appear that the X-rays are some type of wave-motion, or at any rate some kind of pulse with an extended wave-front. Yet after reflection they retain the same corpuscular character which Prof. W. H. Bragg has shown they possess. For the liberation of a high-speed electron from an atom traversed by the X-ray cannot be explained, according to Rutherford, unless it be supposed that the energy of the X-ray is concentrated over a minute volume, and can be given up in an encounter with a single atom. Hence these experiments show that the X-rays possess at the same time the apparently opposite properties of extension over a wave-front and concentration in a corpuscular point.

It appears to the lecturer that the simpler explanation is that we are truly dealing with waves, but that the wave-lengths of the X-rays are excessively short, approaching atomic dimensions, and that the amplitude of the effective waves is actually smaller than the reflecting atom. This view that the X-rays are waves is further supported by the results of some experiments just completed by Barkla, in which a diverging pencil of X-rays was directed on a crystal of rock salt, and the issuing rays received on a photographic plate in the same manner as in the experiments already described. The developed plate shows a new phenomenon, namely, striation of the spots obtained by reflection from the planes of atoms of the space-lattice, especially in the reflections from the cubic cleavage planes. The striations are, in fact, true interference bands, due to interference of the reflections from equally spaced parallel planes of the space-lattice. By the kind courtesy of Prof. Barkla, two of these interesting photographs are projected on the screen. On the assumption that the X-rays are waves, and that the reflecting plane is one passing through corresponding portions of single NaCl molecules—which agrees with the choice of a representative point from each simple molecular grosser unit, or of a similarly situated atom of one of the two chemical elements present in each molecule NaCl to act as such representative point of the space lattice—Barkla has calculated that the wave-length is the one hundred and sixty millionth of a millimetre, $0{\cdot}6 \times 10^{-8}$ mm. If the grosser unit be polymolecular, the wave-length works out larger, being proportional to the cube root of the number of atoms in the molecule. If 8 molecules form the grosser unit of sodium chloride crystals, as suggested by some chemists, the wave-length is found by Barkla to be twice this value, namely, $1{\cdot}2 \times 10^{-8}$ mm.; and if 16 molecules of NaCl are comprised in the grosser unit, as would be the case if Barlow and Pope's structure for the cubic binary compounds be correct (the space-lattice in the case of rock salt being that of the simple cube, No. 1), the wave-length would be still longer, about the seventy millionth of a millimetre, $1{\cdot}5 \times 10^{-8}$ mm. Now it is very interesting that these values are of the same order as those derived from determinations of the velocity of electron ejection, which varied from 1 to 2×10^{-8} mm.

The most trustworthy recent estimations of the size of a molecule of rock salt indicate a diameter about 3×10^{-7} mm. Hence the diameter of a crystallographic molecule 8NaCl would be 6×10^{-7} mm., and of 16NaCl about $7{\cdot}5 \times 10^{-7}$ mm.

It should be emphasised, in concluding the account of this fascinating new field of research, that all these reflections occur in the body of the crystal, and are not surface effects. Cleavage planes usually afford stronger results merely because they are generally primary planes of high reticular density. The effect is sometimes heightened by conducting the X-rays at nearly grazing incidence; but this is by no means necessary, and in Laue's experiments several of the planes were inclined as much as 30° to the incident rays. (See Appendix below).

The experimental proof of the existence of the space-lattice imparts all the more confidence in approaching the other great advance which has lately been achieved. The completion of the catalogue of crystallographically measured substances by Prof. von Groth provokes the question:—What more is needed in order to enable a crystallised substance described in the book to be recognised by means of a few measurements on the goniometer? For it is now proved up to the hilt that, except in the cases of cubic crystals identical in angles in accordance with their perfect symmetry, every solid crystallisable substance is characterised by its own peculiar crystalline form and interfacial angles. This is quite true, even to the last minute of angular measurement, when the conditions of crystallisation are ideal. When thus perfect, even isomorphous substances show differences among themselves to the extent of a definitely measurable number of minutes. But such perfection of growth is not easy to attain, and, in ordinary crystallisation without special precaution against disturbance, is rarely found. The essential crystallographic measurements can, however, be made in an hour's time, provided use be made of the two- or three-circle form

* Prof. T. W. Richards, in the memoir already referred to which has appeared (*Journ. Amer. Chem. Soc.*) since this lecture was delivered and printed, shows how four molecules of zinc sulphide, each composed of an atom of zinc and an atom of sulphur of very different volumes, can form the cubic crystal unit of an edifice possessing cubic systematic symmetry, the different volumes of the two kinds of atoms causing it, however, to exhibit hemihedral class-symmetry.

of goniometer, such as the excellent one devised by Dr. Herbert Smith. This form of goniometer enables all the needful measurements of the interfacial angles to be made with a single setting of the crystal on the wax of the holder. But practical difficulties have hitherto still stood in the way. Excellent as is von Groth's classification—and the most suitable for a work of reference of the full and comprehensive character of this permanent monument of the master's industry and wide knowledge of chemistry, related compounds being arranged and compared in close proximity—the very nature and size of such a work renders it unsuitable for the purpose of discovering rapidly the chemical composition of a substance from its geometrical elements. An index of substances arranged in the order of their symmetry and the numerical values of the crystal constants within the system is what is needed, and this has now for the first time been drawn up for the ten thousand measured substances by Prof. von Fedorow.

Another difficulty then presents itself. It often entirely depends on how a crystal is held in space, that is, which direction in it is to be the vertical axis, which the right-and-left axis, and which the front-and-back axis, as to what the nature of the crystal constants (elements) will be. Moreover, even if two different observers choose these similarly, they may select a different parametral plane (a fourth face other than the three faces parallel to the axes, and cutting off unit lengths from the latter) to determine the axial ratios. Hitherto, beyond a few arbitrary rules—for instance, that the right-and-left axis of a rhombic crystal shall be longer than the front-to-back one—there has been no definite guiding principle for the determination of the setting. Prof. von Fedorow has now given us one, by means of which we can be sure which are the real vertical faces (prismatic or pinakoidal), which is the basal plane (the pair of top and bottom faces), and which set of pyramid faces are the important ones fixing the relative axial lengths. The true setting has been determined by Prof. von Fedorow for every one of the substances in his index, and the crystal elements for such setting calculated.

The mode of classification adopted in this index-catalogue is based on the values of the five fundamental angles which, in general, characterise the crystals of any specific substance. A cubic crystal has definite angles which are entirely fixed and rendered invariable by reason of the perfect symmetry. At the other extreme come triclinic crystals, the general case, in which all five fundamental angles are different and quite independent of each other. On monoclinic crystals there are three independent angles, from which the other two can be calculated. Rhombic crystals have only two independent angles, which, if measured, enable the other three to be calculated. Hexagonal, tetragonal, and trigonal crystals possess only one angle independent of the symmetry, determinative of the relative length of the unique axis of hexagonal, tetragonal, or trigonal symmetry.

The first object of von Fedorow in order to arrive at the correct setting, is to decide which are the primary axial-plane and parametral faces; and he is wonderfully aided here by the discovery of the fact that the faces most extensively developed under ideal conditions of growth are those over which the points of the space-lattice are most densely strewn. Hence, von Fedorow tries to discover the faces of greatest reticular density by calculation. For it is a well-known fact that the most diverse habits—due to different faces being most prominently developed under different conditions of environment—are shown by the crystals of the same substance. A capital example is afforded by the double sulphates of the monoclinic series crystallising with $6H_2O$. One of the commonest of these salts, ammonium ferrous sulphate $(NH_4)_2Fe(SO_4)_2.6H_2O$, exhibits a particular form (consisting of a pair of parallel faces), r' $\{\bar{2}01\}$, not really a primary one, so prominently, the crystals being tabular upon it as illustrated in the lantern slide (Fig. 15), that Wulff has actually taken it as the basal plane, rather than the form c $\{001\}$, which is considered by the lecturer, following older observers, to be the true basal plane for this whole series of isomorphous salts. For the very large development of r' is only a feature of this particular salt of a very large isomorphous series, and the form c $\{001\}$ is in general the plane clearly and prominently announcing itself as the basal plane. The slide (Fig. 16) of a crystal of another member of the series, potassium nickel sulphate, will show this. Hence, Prof. von Fedorow naturally does not rely on the fortuitous relative development of faces, but calculates the relative reticular density of all the principal faces present, in order

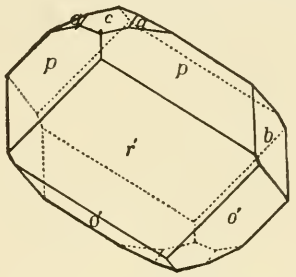

FIG. 15.—CRYSTAL OF AMMONIUM FERROUS SULPHATE.

to discover the true primary faces by their superior reticular density. It has already been shown that we shall have in future an experimental aid in this, in the relative intensity of the spots in the X-ray photographs.

Having thus determined the correct setting, and measured the principal angles, including the five fundamental ones, the results are recorded in the index-table in an abbreviated symbolic form if the substance be a new one, or, if it has previously been measured and therefore appears in his index-table, he discovers the fact at once by the identity of the elements found with those of a substance given in the table. The average time occupied in all this by Prof. von Fedorow or one of his skilled assistants is about two hours. Mr. T. V. Barker, who studied with Prof. von Fedorow before acting as Demonstrator of Mineralogy at Oxford, has been of considerable help in submitting the new method to a very severe test, from which it has emerged with flying colours. He collected, at Prof. von Fedorow's suggestion, fifty specimens of substances which had been crystallographically examined in this country and described in the recognised publications. Five of these were furnished by the lecturer, six

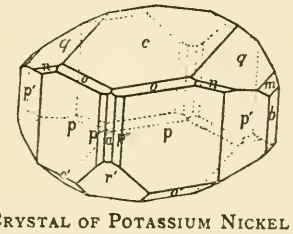

FIG. 16.—CRYSTAL OF POTASSIUM NICKEL SULPHATE.

others by Prof. Armstrong, with the aid of Messrs. Colgate and Rodd, others by Drs. Chattaway and Drugman, and Mr. J. E. Marsh, at Oxford, and the remainder by Mr. Barker himself. Each specimen was only marked by a number, no name or formula being given, on its despatch to St. Petersburg. The result was that Prof. von Fedorow identified without any difficulty 48 of the 50 substances. The crystals of one of the two others were too imperfectly developed to be of use, and the fiftieth specimen was that of a substance which it was afterwards discovered had never hitherto been measured, a fact which was first indicated by its elements not tallying with those of any substance mentioned in the table. This latter occurrence confers even greater confidence in accepting the new method.

It thus appears that in Prof. von Fedorow's hands, or those of his pupils, the method is practically infallible, provided the crystals are well developed and not of cubic symmetry. If the latter perfect symmetry be developed, reference must be made to the optical properties, which the lecturer has always insisted have been far too much neglected, and are here seen to be indispensable. The optical methods, themselves, moreover, as regards their use with small crystals on the polarising microscope, have been further perfected by Prof. von Fedorow, his Universal Stage placing the rapid methods of two and three circle goniometry at the disposal of the microscopist. It must also be remembered that Prof. von Fedorow's method does not discriminate between the members of isomorphous series, as the crystals usually available are not of the high degree of perfection requisite in order clearly to substantiate the last few minutes of any particular angle; for the differences of angle between the members of series formed by metallic family analogues have been shown by the lecturer to be very minute, although unmistakable given the most perfect crystals, and have also been found to obey the law of progression according to the atomic weight of the metal. For instance, ammonium zinc sulphate was simply returned by Prof. von Fedorow as a member of the isomorphous series of monoclinic double sulphates and selenates crystallising with $6H_2O$. Qualitative analysis would be necessary after all, in order to discover the actual member of the series present. Moreover, there are certain features of Prof. von Fedorow's own peculiar version of the theory of crystal structure, such as his idea about pseudo-cubic and pseudo-hexagonal types, and his dealing in consequence with many substances as being deformations of a higher symmetry than they actually show, which to the lecturer appear unnecessary complications likely to discourage the use of the new method. But these defects can, and doubtless will, be eliminated as the method becomes practically applied.

In conclusion, it must be obvious that a great advance has really now been made in crystallography. For the geometrical conception of crystals as homogeneous structures, based on the 14 space-lattices as the grosser structures and the 230 point-systems as the ultimate atomic structures, has been not only theoretically perfected, but proved by direct experiment to represent the actual fact, by the epoch-making work of Laue, Friedrich, and Knipping. The descriptions and chemical relationships of all the ten thousand measured substances have been brought together in the great book of Prof. von Groth, and the material further sifted, reduced to correct setting, and arranged according to symmetry and elements by Prof. von Fedorow, in a tabular form immediately available as a reference index for identification purposes, thus providing the material for a true crystallo chemical analysis. The science of crystallography is thus now placed on a secure foundation, supported equally by mathematics, geometry, and experiment, and its natural data are rendered available for chemists and physicists alike.

It must be obvious that these significant results place the science in such a strong position that it can no longer be ignored as in the past by both physicists and chemists, and that to both an elementary knowledge of the subject will be imperative and absolutely indispensable in future. That crystallochemical analysis will ever replace qualitative chemical analysis is neither to be expected nor desired, even if alone on the ground of the admirable training and experience in chemical operations and principles which chemical analysis affords. But so powerful an aid cannot with impunity be neglected, and the knowledge of crystallography required of the chemist who desires to be armed with the new weapon of research will be of the utmost benefit to him, in the sense of giving him a wider grasp of the nature both of the particular chemical solid matter under his own immediate investigation, and of the nature of solid matter, the most highly organised of all the forms of matter, in general.

Appendix.

Since this lecture was delivered, the following further experiments with X-rays and crystals have been described in *Nature* (1913, xci., pp. 111, 135, and 161). H. B. Keene has obtained with crystals of galena, mica, and rock salt results analogous to those of Laue, Friedrich, and Knipping, the spot diagrams corresponding to the holohedral systematic symmetry in each case. T. Terada has found that the transmitted rays may be rendered optically visible by means of an ordinary fluorescent screen, provided the pencil of rays be from 5 to 10 mm. in diameter and the crystal adequately transparent to the rays; this latter he found to be the case with crystals of alum, borax, cane-sugar, fluorspar, mica, rock crystal, and rock salt, in thicknesses of 4 to 10 mm. M. de Broglie has obtained spot diagrams similar to those of Laue, Friedrich, and Knipping, with fluorspar, magnetite (using an octahedron face), and rock salt; but all the spots were striated with parallel fringes. Finally, Owen and Blake have obtained what appears to be a line spectrum of X-rays by using the surface of a crystal of gypsum as a diffraction grating. The lines were always the same with different crystals, using the same X-ray bulb, but the different lines varied in intensity with the hardness (degree of vacuum) of the bulb. The evidence from the action of crystals on X-rays is thus accumulating that the X-rays are waves of exceedingly short wave-length.

METHODS OF SEPARATING NIOBIUM AND TANTALUM PARTICULARLY BY MEANS OF POTASSIUM CHLORIDE IN HYDROFLUORIC ACID SOLUTION.

By Dr. EUG. MEIMBERG and PAUL WINZER.

Since tantalum metal has been manufactured technically the complete separation of niobium from tantalum has acquired increased importance. The presence of niobium has a great influence on the properties of tantalum.

Good results are generally obtained by Marignac's method of separation, especially in the form described by one of us (Meimberg, *Angew. Chem.*, 1913, [1], xxvi., 83). But it suffers from the disadvantages that, firstly, large quantities of the material under investigation must be used, and, secondly, it is complicated owing to the numerous crystallisations.

Unlike Wedekind and Maas (*Angew. Chem.*, 1910, xxiii., 49) we could not obtain satisfactory results by Weiss and Landecker's method, precipitation of alkali solution by means of carbon dioxide (*Zeit. Anorg. Chem.*, 1913, lxiv., 65). Both the residue obtained by opening up the material and the extracting with water, and also the crystals which separate from the solution, contained niobium. By means of carbon dioxide niobic acid is precipitated from the solution together with tantalic acid. Niobium was determined colorimetrically in the different phases of the precipitation (Meimberg, *Angew. Chem.*, 1913, [1], xxvi., 83). The results obtained were no better when Hauser and Lewite's (*Angew.*, 1912, xxv., 100) modification was employed, in which potassium nitrate, the addition of which appears to be unsuitable, is not used. We consider the method inapplicable both in analytical and preparative work.

Our attempts to separate niobium by a simple method were based, first, upon the property of niobic acid of dissolving in certain acids (oxalic acid, hydrochloric acid), thus differing from tantalic acid.

The ore was completely opened up with caustic alkali, the melt taken up with water, and the oxides of iron and manganese were filtered off. The dissolved potassium salts of tantalum and niobium were precipitated as the insoluble sodium salts by means of soda, and the precipitate was introduced into a boiling concentrated solution

of oxalic acid. The result was not satisfactory. The potassium salts of tantalic and niobic acids are in themselves readily soluble when freshly prepared. However, the solution of the potash melt of niobic and tantalic acid occurs with partial decomposition of both salts. When ore is used this decomposition is considerable; thus 25 per cent of the tantalic acid of a 63 per cent tantalite remains behind in the sediment containing iron and manganese. The solubility of niobic acid in oxalic acid was greatly reduced by the presence of tantalic acid; thus 30 grms. of oxalic acid had dissolved only 1 grm. of niobium, while by itself 1 grm. of niobic acid would require only 1·5 grm. of oxalic acid.

There seemed to be a better chance of success if advantage were taken of the property of niobic acid (when freshly precipitated from niobates) of going into solution in considerable quantities when it is boiled for about half-an-hour with concentrated hydrochloric acid and then diluted with water. But here again it was found that niobic acid loses its solubility when in combination even with small quantities of tantalic acid. This explains the statements in literature, that niobic acid is insoluble, or only slightly soluble, in hydrochloric acid; the niobic acid used was not absolutely free from tantalum.

The lower oxides of niobium, obtained by reduction of freshly precipitated niobic acid with zinc and hydrochloric acid, are very readily soluble in hydrochloric acid, and thus appear to be more applicable than niobic acid for the separation from tantalic acid. But once again the solubility entirely disappears in presence of tantalic acid. The result obtained by using the dissolved double fluorides of the two acids was no better. Niobium potassium fluoride was easily reduced, while tantalum potassium fluoride was not. The product of reduction was precipitated with ammonium, when the lower niobium oxides remained unchanged, and then it was heated to boiling with concentrated hydrochloric acid, care being taken to avoid oxidation. No solution occurred, and both metals were obtained in the form of pentoxide.

We then returned to separation by the potassium fluoride double salts.

If a solution of potassium fluoride or difluoride is added little by little until it is present in excess to a solution of a columbite in hydrofluoric acid, a dirty brown precipitate of potassium tantalum fluoride is obtained from the first moment right on to the end; it contains also niobium, iron, and manganese. If, however, a solution of pure niobic and tantalic acid is precipitated similarly, much less niobium is carried down. Iron and manganese seem to form double salts with niobium and tantalum fluoride, which are isomorphous with tantalum potassium fluoride and crystallise with it on precipitation. Our first effort was therefore directed towards keeping the iron and manganese in solution, or excluding them, during the precipitation. For this purpose we first added concentrated hydrochloric acid to the raw ore-liquor. (When the temperature is raised hydrochloric acid increases the solubility of potassium tantalum fluoride, but on cooling the solubility is only very slightly raised). It was then precipitated in the warmth with a saturated solution of potassium difluoride. In spite of the addition of large quantities of hydrochloric acid all stages in the precipitation contained niobium, iron, and manganese.

Iron and manganese were now salted out by means of ammonium fluoride from hydrofluoric acid solutions of tantalite and columbite, but in a liquid treated thus the precipitation of niobium by means of potassium difluoride was not satisfactorily prevented.

These results convinced us that by precipitation with potassium difluoride only a gradual separation can be effected by means of repeated crystallisations, and we then had recourse to precipitation with other potash salts, *e.g.*, potassium sulphate and chloride, giving the preference to the more soluble chloride. We hoped that the liberation of hydrochloric acid *in statu nascendi* would keep the niobium, iron, and manganese in solution more effectually, and particularly that the velocity of the reaction would be considerably lowered. Our expectations were fulfilled. The requisite quantity of a concentrated potassium chloride solution was added to a warmed solution of columbite in concentrated hydrofluoric acid, which contained all the niobium, iron, and manganese in the ore. It was then allowed to cool and the potassium tantalum fluoride gradually separated. The residue obtained after cooling was perfectly white and contained only small quantities of niobium, iron, and manganese. In an experiment with a mixture of equal parts of pure niobic and tantalic acids the product of the precipitation contained only very small quantities of niobium, which could be removed by one crystallisation. It was thus found that the solubility of potassium tantalum fluoride in presence of an excess of potassium chloride in the mother-liquor is much less than in excess of KF or KHF_2. The precipitation was found to be quantitative. Potassium tantalum fluoride is salted out almost quantitatively from its aqueous hydrofluoric acid solution by the addition of potassium chloride. Almost the same result was obtained by precipitation with a solution of potassium fluoride containing a sufficient quantity hydrochloric acid. Potassium chloride is thus formed, and the action is the same as before.

Thus precipitation with potassium fluoride may be regarded as a direct action of this salt on tantalum fluoride, when all the potassium fluoride present enters into reaction at once, while when potassium chloride is used the formation of potassium tantalum fluoride is dependent on the potassium and fluorine ions present. The formation of the more readily soluble double salts can take place only after the complete precipitation of the tantalum.

For quantitative analysis we proceed as follows:—About 30 grms. of the ore are opened up in potassium bisulphate. It is hardly possible to prevent spirting in this operation, and hence it is advisable to use this large quantity of ore in order to reduce the error.

The metallic acids obtained after boiling are subjected to the necessary treatment to remove other elements. An aliquot part of the purified acids, about 5 to 10 grms., is taken for the separation of the niobium. It is dissolved in hydrofluoric acid (using the quantity necessary for the formation of the potassium double fluorides), a saturated solution of potassium chloride is added in excess, and the whole is allowed to cool. The total quantity of liquid is chosen so that the potassium niobium fluoride formed can remain in solution. (Solubility of potassium niobium fluoride in water 1 : 12). The potassium tantalum fluoride obtained is converted into acid by evaporation with sulphuric acid, and this is again precipitated from hydrofluoric acid solution by means of potassium chloride solution. The total quantity of liquid is kept much smaller than in the first precipitation in consequence of the small amount of niobium. The potassium double fluorides of both precipitations are washed with a cold potassium chloride solution. The tantalic acid must not be calculated from the fluorides but must be determined as acid.

The method is still simpler if the potassium tantalum fluoride first obtained is dissolved in water containing hydrofluoric acid, to remove the last traces of niobium, then potassium chloride solution is added, and the liquid is allowed to get perfectly cold. The precipitation of the potassium tantalum fluoride occurs nearly quantitatively as before, while the niobium is kept in solution. The crystallised potassium tantalum fluoride is converted into tantalic acid by evaporation with sulphuric acid, it is boiled with water containing hydrochloric acid and with ammonia, and weighed as Ta_2O_5. The absence of niobium in the potassium tantalum fluoride obtained must be determined colorimetrically in an aliquot part before it is decomposed (*Angew. Chem.*, 1913, [1], xxvi., 83). The niobic acid is determined in the liquors (*Angew. Chem.*, 1913, [1], xxvi., 83). Titanic acid (*Angew. Chem*, 1913, [1], xxvi., 83) must be determined colorimetrically in the acids obtained and deducted.

This method, on account of its comparative simplicity

and good yield, is very suitable for the manufacture on the large scale of tantalic acid or its compounds from ores. The finely powdered ore, columbite or tantalite, is dissolved in an equal quantity of concentrated raw hydrofluoric acid in a metal vessel or wooden barrel lined with caoutchouc, the pressure being raised to 3 or 4 atmospheres and the whole continuously stirred.

The clear liquors are warmed with steam and precipitated with a saturated potassium chloride solution, and for this purpose the quantity of potassium chloride is taken which is necessary for the precipitation of the tantalic acid only. It is thus possible to work with concentrated solutions. The tantalic acid obtained from the potassium tantalum fluoride is subjected to the purification which is necessary in view of the impurities and then again precipitated from hydrofluoric acid solution with potassium chloride. Before the precipitates are removed each time potassium chloride and hydrofluoric acid are used to test whether the precipitation of the potassium tantalum fluoride is complete. The quantities of hydrofluoric acid and potassium chloride necessary are easily determined previously by removing a measured quantity and testing it. If the work is carefully done, even when very large amounts are used the potassium tantalum fluoride thus obtained is almost free from niobium. To obtain a salt which is perfectly free from niobium it is subjected to one more crystallisation from water containing hydrofluoric acid, and then some hydrochloric acid is added to increase the solubility; in this case also metal vessels lined with rubber can be used.—*Zeitschrift für Angewandte Chemie*, 1913, xxvi., 157.

MANUFACTURE AND USES OF CYANAMIDE.*

By E. J. PRANKE.

(Concluded from p. 293).

Preparation for Use as a Fertiliser Material.

THE crude cyanamide obtained from the nitrifying ovens, after cooling, is crushed to a fine powder, and is passed into rotating, slightly inclined, steel cylinders, in which it is treated with sufficient water to eliminate the carbide and to slake the calcium oxide. A further slight addition of water is made before the material is run through briquetting machines.

The resulting bricks harden rapidly and are stored until they can be crushed just prior to shipment. Crushing is done in a series of rolls with intermediate screens, the final product having a coarseness of about 15- to 50-mesh screens. It is packed in ordinary fertiliser bags and distributed in carload lots to manufacturers of mixed fertilisers. The material so prepared contains nitrogen equivalent to about 19 per cent ammonium.

It analyses approximately as follows:—

	Per cent.
Calcium cyanamide	45
Calcium carbonate	4
Calcium hydroxide	27
Calcium sulphide	1
Free carbon	14
Iron and alumina	2
Silica	2
Combined water	4
Free moisture	1

Uses of Cyanamide.

At present, cyanamide is used in this country principally for agricultural purposes. It is known to have a fertilising value equal or superior to that of other common products used for the same purpose. Some of the earlier experiments with this material indicated an uncertain action on very acid moor soils, but the same thing is true of other fertilisers requiring nitrification prior to absorption by the plant, and is the fault of the soil and not of the fertiliser. Such soils must be restored to normal condition before fertilisers can be expected to have their full effect. In other cases, experimenters applied quantities far in excess of those used in practical agriculture, and obtained a lower efficiency of utilisation than with the normal applications. As a general conclusion from the hundreds of recorded experiments and from the testimony of practical agriculturists, it may be said that when cyanamide is used in the same way as other fertilisers are used in ordinary practice, its efficiency of utilisation is about the same as that of the high-grade fertiliser materials, and superior to that of the low-grade fertiliser materials.

The particular advantage of cyanamide as a fertiliser material lies in the advantageous effects that follow its admixture with other constituents of complete fertilisers. It greatly improves the mechanical condition of such mixtures, and by its alkaline properties prevents the escape of valuable nitrogen oxides and of bag-rotting hydrochloric acid, set free by the action of free acids in acid phosphate upon nitrates and chlorides in the mixtures.

Statements have been made that there is a loss of ammonia from cyanamide during long-continued storage. It has been found, indeed, that the nitrogen percentage in stored material does decrease, especially in very damp climates, but it has been determined by very careful experiments, both on a small scale and on a large scale in fertiliser factories, that such decrease in the nitrogen percentage is due not to any actual loss of nitrogen, but to the increase in the weight of the material, due to its absorption of carbon dioxide and of moisture from the atmosphere. Part of the moisture absorbed is fixed chemically into forms from which it is not recovered on heating in a drying oven, hence it is necessary, when testing the storing qualities of this fertiliser, to weigh the material before and after the period of exposure and to determine the nitrogen percentage each time.

Soil Action of Cyanamide.

It has been definitely established by the researches of Ulpiani and Kappen, among others, that cyanamide applied to the soil is completely converted in the course of a few days into urea, by the catalytic action of the colloids and other constituents of the soil, in accordance with the following reactions: $CaCN_2 + 2H_2O = Ca(OH)_2 + H_2CN_2$, $H_2CN_2 + H_2O = CO(NH_2)_2$.

The urea is further converted by bacterial action and possibly by chemical processes into ammonia, which further reacts with zeolites, humates, and other soil constituents, to form double ammonium salts, that are retained as a part of the soil until further bacterial action or the solvent effect of plant roots makes them available to vegetation. Cyanamide is said to be completely utilised by the crop in from 60 to 80 days.

Other Uses.

When cyanamide is subjected to the action of superheated steam under pressure of several atmospheres, it is converted almost quantitatively into ammonia and calcium hydroxide. It thus serves as a convenient and cheap source of pure ammonia. By the Ostwald process, which uses thoria and ceria as catalytic agents, ammonia can be commercially converted into nitric acid.

By fusion of cyanamide with alkaline salts in the presence of carbon, cyanides are easily produced and can be separated and purified as desired.

When cyanamide is extracted with water between 70° and 100° C., nearly all of the nitrogen is converted into dicyandiamide $(H_2CN_2)_2$. This compound is used in the dye industry and also in the explosives industry in place of ammonium oxalate, to reduce the temperature of the explosive gases.

Other derivatives, such as urea, guanidin and its salts, and various dicyandiamidin salts, are now being manu-

* Address before the Nashville Section of the American Chemical Society. From the *Chemical Engineer*, xvii., No. 3.

factured in Germany. One or both of the hydrogen atoms in the amide group in cyanamide, $CN.NH_2$, can be replaced by metals, alkyl or aryl groups, alcohol groups, aldehyde groups, and others, thus leading to an immense number of organic derivatives. The possibilities in this field have been investigated but little.

Various compounds of cyanamide, and its derivatives, with alkaline salts and carbonaceous materials, are made and sold in Germany under the names of ferrodur, intensit, hesolin, and others. These compounds, known as "hardening" or "cementing" powders, are used in place of cyanides, ferrocyanides, waste leather and similar materials, for case-hardening of steels. These products containing cyanamide are not only cheap, but they are efficient for the purposes for which they are intended.

Future of Cyanamide Industry.

The cyanamide industry is undoubtedly only in its nfancy. At present there are four factories in Germany, our in Italy, two in France, and one each in Austria, Norway, Sweden, Switzerland, Japan, and America. The American Cyanamide Company built its first plant at Niagara Falls, Ontario, in 1909, beginning commercial manufacturing January 1, 1910. Additions to the plant, which were completed in March, 1913, will give a capacity of 25,000 tons per annum, and by the end of the year the full productive capacity of the company, including the extensions now under way, should be 50,000 tons per annum.

THE SCIENTIFIC WEEK.

(From Our Paris Correspondent).

A New Method of Treating Trees.

A new method of treating trees has just been inaugurated by an arboriculturist, M. Simon. M. Simon has treated an apple-tree by intravenous injections and the apple-tree is cured. This tree which was languishing was regenerated. In the same way as injections of physiological serum or sea-water give strength and new life to debilitated or anæmical children, so trees regain their vigour by injections of pure water. After the injections of pure water M. Simon made punctures in the tree of water mixed with liquid dung, then with water mixed with various salts: nitrate of potash, sulphate of potash, precipitated phos phate, ordinary kitchen salt, &c. This medication cured the tree in less than twenty days. It had absorbed more than three litres of these different liquids. The apple-tree then formed buds and developed leaves, and in less than six months its branches had increased from 20 to 25 centimetres.

Another apple-tree which was in a far worse state of health, all dried up and black, ready to be burnt, absorbed in less than two days three litres of dung diluted with nitrate of soda, nitrate of potash, and phosphate. The tree recovered and bloomed splendidly.

Peach-trees treated in the same way bore superb fruit, while neighbouring peach-trees were in a bad state.

These experiments confirm those of Dr. Mokrzecki, who thought of introducing pieces of sulphate of iron into trees suffering from chlorosis, and which were thus radically cured.

"The Aviette."

If the apparatuses heavier than air have shown what they are capable of, whether they be monoplanes or biplanes, the same cannot be said of the "aviette"; that is to say of that little aeroplane which is said to be susceptible of flying in using only the simple energy or force exerted by man. It is one of the problems of the moment the solution of which is being passionately sought for.

M. Magnan, Director of l'Ecole des Hautes Etudes, in a notice presented recently to the Academy of Science by M. Ed. Perrier, Director of the Paris Museum, has calculated the characteristics that should be possessed by an "aviette" weighing 100 kilogrms. with its pilot, which represents a minimum weight. He has found, admitting that the "aviette" was soaring apparatus like the monoplane—

	Minimum.	Maximum.
Alary surface	3·04 m².	4·98 m².
Weight of wings ..	15·630 kgs.	19·700 kgs.
Total spread	4·91 m.	6·17 m.
Width of wing.. ..	1·11 m.	1·19 m.
Total length	2·75 m.	3·06 m.

To establish these maxima dimensions M. Magnan has utilised documents supplied to him by the soaring birds, the birds of prey. These minimum figures have been obtained by calculating the data of the "aviette," starting from the group of crows whose relative alary surface is already sufficiently small not to allow any easy soaring flight. An "aviette" wishing to copy soaring birds must then, for a weight of 100 kilogrms. in travelling order, possess characteristics superior to the dimensions of crows. Its stability will be so much the greater as these characteristics are nearer those of the dimensions of soaring rapacious birds.

But there is one important question to be answered. Will a man be capable of moving an apparatus with the mere help of his own muscles?

It will be necessary to study the maximum force that can be expended by a man fully trained to sport, a cyclist for example, and then to find out if his energy would be sufficient to raise such an "aviette." From that moment the dream of Icarus would be realised.

A New Method of Clinical Analysis.

The study of capillary phenomena formerly permitted M. Lippmann to construct one of the most practical and most precise electrometers that is in existence. In a recent work, M. Dubrisay, Doctor of Science, and Engineer of the School of Arts and Manufactures, shows the possibility of using analogous principles for the bases of a method of chemical analysis of an extreme sensibility.

As his point of departure, M. Dubrisay has taken the lowering of superficial tension by a trace of alkali on the surface of separation of water and vaseline oil holding a fatty acid in solution (oleic or stearic).

This lowering measured by the method of a drop-counter is considerable; the number of drops of oil pass from 72 in pure water to 107 in water mixed with 0·004 molecule of soda per litre.

M. Dubrisay has, in this way, studied the neutralisation of different mineral or organic acids. The stability or the hydrolysis of the salts formed is shown with great clearness. The method is at least as sensitive as that of electric conductibilities; it only requires a rudimentary apparatus and presents no difficulty in its application.

A Prehistoric Census.

It is doubtless somewhat bold, at the distance at which we are to-day, to wish to make a census of prehistoric humanity. However, one can but try the essential being to be aware that one can only succeed in a certain and weak measure.

That is what M. Rutot, the well-known Belgian geologist and prehistorian, has done. He has tried to make out what was the probable figure of the population of Belgium at the end of the palæolithic period. There are a good number of caves in Belgium, but not the half of them were ever occupied (it was more easy to find house room than to-day), and moreover the number of periods of habitation was eight, and they must be kept quite distinct and separate.

The principal immigration into Belgium seems to have taken place during the lower Aurignacian, a period to which belong five caves, which would support fifty or sixty persons. For the stations in the open air would only have been temporary and not places of habitation; they would never have had any sedentary population.

During the Magdalenean period the number of the population seems to have been more considerable, and probably went up to sixty. At the end of this period, humanity (abandoned by the reindeer that went up towards the North, following the receding ice) quitted the shelters that a milder climate rendered less necessary, and settled on the banks of the lakes of Campine, and at the dawn of the Neolithic period Belgium contained 100 or 150 inhabitants.

Later on another factor allowed of the establishment of a more numerous population; the Cervides forests, thanks to which there were something like a thousand inhabitants. And at the beginning of the age of polished stone the country might perhaps have contained four or five thousand inhabitants.

The Rôle of Chlorophyll.

By numerous experiments presented to the Academy of Science by M. Mangin, M. Dangeard has shown how a colouring substance such as chlorophyll can serve as an intermediary between the solar energy that it absorbs and the substances that are found mixed with it. These substances utilise, for their own chemical transformations, the radiations which would have no action on them if they were isolated. It is thus easier to understand the part played by chlorophyll in the assimilation of carbon by plants, and one can thus foresee the possibility of reproducing outside the vegetable cellules the principal phenomena of the chlorophyllian synthesis.

The Tin-ware Industry in Germany.

Tin-ware is of German origin, and seems to have been manufactured for the first time in the Fichtel Gebirge. The industry afterwards spread into Silesia, Bavaria, and especially into Saxony. But from the beginning of the eighteenth century English manufacturers established factories of the new metal in Wales. Their progress was so considerable that a century later the German manufacturers had disappeared one after the other, and Germany had become the customer of England.

Toward the middle of the nineteenth century Rhenish and Westphalian manufacturers took up again the fabrication of tin-ware, and created a cartel January 26, 1862, of which M. Lohse thus relates the history. Until 1873 the cartel was prosperous, the economical crisis and the lowering of the custom duty—which from 30 francs per 100 kilogrms. in 1865, fell to 2 francs 50 in 1873, to disappear entirely in 1875—stopped the flight of the industry, which till 1895, in spite of the increase in the production, did not manage to remain mistress of the national market; the English importation became more and more important. This latter, driven from the American market by the prohibitive custom tariffs, had to dispose of its surplus production in Germany in spite of the establishment of a duty of 6 francs 25 per 100 kilos. in 1879. At last the cartel reformed more solidly in 1895 has reconquered the national market.

During this period of fifty years, the German production has passed from 50,000 cases in 1862 to 1,100,000 in 1911. The prices have gone down by half; from 87 francs per 100 kilos. in 1862 they have fallen to 43 francs in 1910.

Fluorides of Osmium.—Otto Ruff and Friedrich Wilhelm Tschirch.—Osmium forms three fluorides, OsF_8, OsF_6, and OsF_4. The octafluoride is formed when osmium is heated to 250° in a current of fluorine, and some osmium hexafluoride is also obtained as a by-product. Osmium tetrafluoride is found in the residue, with some unchanged osmium, if the action of the fluorine is incomplete. The octafluoride is a crystalline lemon-coloured substance which darkens to reddish yellow above 34·5°. Its vapour is colourless. It readily attacks metals and organic substances. — *Berichte*, 1913, xlvi., No. 5.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, June 12th, 1913.

Sir Archibald Geikie, K.C.B., President, in the Chair.

Commendatore Giacomo Boni gave an Address on Recent Researches on the Palatine, in relation to Geology, Ethnology, and Physics.

Papers were read as follows :—

"*Growth and Sporulation of the Benign and Malignant Tertian Malarial Parasites in the Culture Tube and in the Human Host.*" By J. G. Thomson, M.A., M.B., and D. Thomson, M.B.

"Plasmodium cephalophi *Sp. nov.*" "*Trypanosome causing Disease in Man in Nyasaland.*—II. *Susceptibility of Animals to the Human Strain.*" "*Trypanosome Diseases of Domestic Animals in Nyasaland.*—I. Trypanosoma simiæ *Sp. nov.* Part II. *Susceptibility of various Animals to* Trypanosoma simiæ." "*Trypanosome Diseases of Domestic Animals in Nyasaland.*—I. Trypanosoma simiæ *Sp. nov.*" Part (III.). By Surgeon-General Sir David Bruce, F.R.S., Majors D. Harvey and A. E. Hamerton, and Lady Bruce.

CHEMICAL SOCIETY.

Ordinary Meeting, June 5th, 1913.

Prof. W. H. Perkin, LL.D., F.R.S., President, in the Chair.

(Continued from p. 296).

163. "*The Estimation of Nitrites by means of Thiocarbamide, and the Interaction of Nitrous Acid and Thiocarbamide in Presence of Acids of Different Strength.*" By May Emily Coade and Emil Alphonse Werner.

In continuation of work already published (*Trans.*, 1912, ci., 2180), experiments have been carried out to test the value of thiocarbamide as a reagent for the estimation of various nitrites. The results have shown that thiocarbamide is a reagent superior to any of those which have been employed hitherto in the estimation of nitrites by the gasometric method. The advantages of the method are as follows: —

1. The accuracy of the results are not affected by the presence of nitrates, even when in large excess.

2. Analyses can be completed in a few minutes; no subsequent manipulation of the evolved gas is necessary as when carbamide is used; the chances of experimental error are thereby reduced.

3. The gas can be read off with great accuracy; even after a large number of analyses the mercury in the nitrometer remains quite untarnished, which is not the case in other methods.

4. A much larger number of analyses can be made in a given time than by the other methods; two minutes suffice for the complete evolution of the gas (nitrogen) when acetic acid is used; by the carbamide method twenty-eight minutes were required to complete the reaction.

In the presence of a weak acid, the change takes place according to equation (*a*), in the presence of a strong acid according to equation (*b*): -

$$(a)\ CSN_2H_4 + HNO_2 = HSCN + N_2 + 2H_2O.$$

$$(b)\ 2CSN_2H_4 + 2HNO_2 = C_2S_2N_4H_6 + 2NO + 2H_2O.$$

The total volume of gas evolved is the same in each case for the same weight of nitrite used.

The influence of a number of acids on the direction of the change was examined. It was shown that the reactions (*a*) and (*b*) proceed simultaneously according to the nature of the acid used, and the direction of the change on the

lines of equation (*b*) was found to be directly proportional to the dissociation constants of the acid.

164. "*A Case of Isomerism in the Methylated Ferrocyanides.*" By Ernald George Justinian Hartley.

Further experiments on the preparation of tetramethyl ferrocyanide by heating hexamethylferrocyanogen chloride show that the former compound is thereby produced in two forms, having the same percentage composition and molecular weight, but exhibiting quite distinct properties.

165. "*Preparation of Secondary Amines from Carboxylic Acid.* Part III. *Disecondary Amines from Dicarboxylic Acids.*" By Henry Rondel Le Sueur.

The α-anilino- and α-1- and α-2-naphthylamino-derivatives of dicarboxylic acids, when heated above their melting-points, readily lose two molecules of carbon dioxide with the formation of the corresponding secondary amines. Thus, a 69 per cent yield of *s*-diphenyloctamethylenediamine is readily obtained from αθ-dianilinosebacic acid:—

$$CO_2H\cdot CH(NHPh)\cdot[CH_2]_6\cdot CH(NHPh)\cdot CO_2H \xrightarrow{\text{heat}} NHPh\cdot[CH_2]_7\cdot NHPh.$$

The results obtained show that the method is of general application, and very suitable for the preparation of the alkyl derivatives of aniline and naphthylamine.

166. "*Guanidine Thiocyanate: its Formation from Ammonium Thiocyanate.*" By Hans Krall.

Guanidine is produced when ammonium thiocyanate is heated beyond the temperature at which thiocarbamide is formed. The equations usually given to explain the change appear to be purely hypothetical, and no careful experiments seem to have been made with the view of establishing the mechanism of the process.

It was shown that the thiocarbamide first formed partly decomposes into hydrogen sulphide and cyanamide, the latter uniting with unchanged ammonium thiocyanate to form the guanidine salt. The volatile products are hydrogen sulphide, ammonia, carbon disulphide, and the products of interaction of these. The carbon disulphide results from the interaction of hydrogen sulphide and thiocyanic acid, $H_2S + HNCS = NH_3 + CS_2$.

Since thiocarbamide dissociates into ammonia and thiocyanic acid in its reversion to ammonium thiocyanate (Werner, *Trans.*, 1912, ci., 2186), the suggestion was made that at higher temperatures it tends to change partly into the isomeric form, $NH{:}C(SH)\cdot NH_2$, which could dissociate into hydrogen sulphide and cyanamide.

It was found that the best conditions for the preparation of guanidine consisted in heating dry ammonium thiocyanate for four hours at 200°, when a yield of 60 per cent was easily obtained. The conditions usually stated, namely, 180—190° for twenty hours, are unduly tedious, and have no compensating advantage.

"167. "*Silicon Compounds.* Part I. *Rational Nomenclature of Complex Silicon Compounds and Silicates, both Organic and Inorganic.*" By Geoffrey Martin.

The author explained a scheme for classifying the compounds of silicon on the basis of the number of linkings between the silicon atoms in the molecule. Compounds in which the silicon atoms are directly united are termed "*silicoses*," whilst those in which the silicon atoms are joined up through oxygen, thus Si·O·Si, are termed "*silicates.*"

168. "*Silicon Compounds.* Part II. *Methylsilicoses Derived from Silicon Hexachloride.*" By Geoffrey Martin.

The author described compounds derived from the action of magnesium methyl iodide on silicon hexachloride, which contain silicon atoms directly united in a chain, and dissolve in potassium hydroxide evolving hydrogen. They also evolve a mixture of hydrogen and methane when heated.

169. "*The Synthesis of* o-*Aldehydophenylglycine.*" By Wilhelm Gluud.

o-Aldehydophenylglycine, which the author considered might prove a suitable source for the production of indole or its derivatives, was synthesised in the following way:—

Starting with *o*-nitrobenzaldehyde, by reducing the corresponding oxime with ammonium sulphide, *o*-aminobenzaldoxime was obtained. The latter compound, when heated with chloroacetamide and calcium carbonate, yielded the *oxime* of o-*aldehydophenylglycinamide*, which, on boiling with alkali, gave the *oxime* of o-*aldehydophenylglycine*. The oxime group was removed by dilute sulphuric acid, yielding o-*aldehydophenylglycine* $CHO\cdot C_6H_4\cdot NH\cdot CH_2\cdot CO_2H$. The pure dry compound consisted of aggregates of colourless crystals, melting at 176—177°.

When heated with lime, either the aldehyde or the oxime of *o*-aldehydophenylglycinamide yielded indole or its derivatives; this reaction will be further investigated.

A crystalline compound, supposed to be *o* cyanophenylglycine, was prepared from the oxime of *o*-aldehydophenylglycinamide and sulphuric acid.

By the fusion of the oxime of *o*-aldehydophenylglycine or the corresponding amide with potassium hydroxide, phenylglycine-*o*-carboxylic acid and indigotin were produced in quantities depending on the experimental conditions.

170. "*Colour and Constitution of Azomethine Compounds.*" (Part III.). By Frank George Pope and Winifred Isabel Willett.

Unsuccessful attempts have been made to obtain azomethine compounds from *p*-nitroaminoazobenzene. Various derivatives of aminoazobenzene were described, together with some compounds related to *p*-nitroaminoazobenzene. *p-Nitrobenzeneazobenzeneazophenol* has been prepared, and the absorption spectra of the azomethines derived from aminoazobenzene, together with those of *p*-nitrobenzeneazophenol and *p*-nitrobenzeneazobenzeneazophenol, have been observed.

171. "*Note on Cupric Malate and Citrate.*" By Spencer Umfreville Pickering.

When alcohol is added to a solution of copper carbonate in glyceric, malic, or citric acid, it precipitates an emulsion, which dries to a pale blue solid, very soluble in water, forming a dark blue solution, in which the copper, on electrolysis, is found to be in the electro-negative ion. The compound present is a cupri-compound metameric with the normal cupric salt, which latter, in the case of the glycerate, crystallises gradually from the solution, and is sparingly soluble. Normal cupric malate has now been obtained in the same way, and is insoluble, but the presence of some excess of acid is necessary to prevent the formation of a basic salt. The normal citrate has not been obtained; a concentrated solution of the cupricitrate solidifies in ten minutes to a mass of blue, moderately soluble crystals of (probably) a basic cupric-compound, $(R'''_2Cu_3)_2,CuO$, which, after thirty minutes, changes to an insoluble amorphous, ordinary basic salt of the same empirical formula.

172. "*Organic Ferric Salts.*" By Spencer Umfreville Pickering.

The quadrivalent character of copper in the cupri-compounds is supported by the similarity between these and the salts of quadrivalent iron. In the latter the iron is electro-negative, does not react as iron with ordinary reagents, and has a colour intensity about twenty times greater than that of iron in inorganic ferric salts. They are very soluble, and alcohol precipitates emulsions from them. Evidence as to the definiteness of their composition was given. In the case of the tartrate, malate, and citrate, the corresponding normal salts have not been obtained, but they each yield a highly soluble basic ferri-compound, R''_3Fe_2,Fe_2O_3, and an insoluble ordinary basic salt of the same formula, thus resembling the cupricitrate. Ferric oxalate is a normal salt, and the acetate appears to

be dissociated in solution into acetic acid and colloidal ferric hydroxide. Attempts to prepare alkaline ferri-compounds have failed.

173. "*The Colour Intensity of Iron.*" By Spencer Umfreville Pickering.

The molecular colour intensity of iron in solutions of ferric chloride, nitrate, and sulphate is practically identical (taken as unity), and is nearly constant throughout a considerable range of strength. It gradually rises to 2·5, after which further dilution causes it to fall; but these dilute solutions are not stable, and darken gradually, ultimately exhibiting a colour intensity of 140, which is that of iron in colloidal ferric hydroxide. This first rise to 2·5 is not due to the presence of colloidal iron, but to iron in some other highly coloured form, probably that in which it exists in organic ferric salts, where it is electro-negative, and has a colour intensity of 24. This value is nearly realised in the case of the sulphate. As excess of acid in the case of the sulphate and nitrate render these salts colourless, it is probable that the true colour intensity of electro-positive iron is nil, the yellow colour of the neutral salts being due to the presence of some of the compounds with the iron electro-negative.

174. "*The Conversion of α-Amino-acids into α-Ketonic Aldehydes, and their Relation to α-Hydroxy-acids.*" By Henry Drysdale Dakin and Harold Ward Dudley.

The authors have recently shown (*Proc. Chem. Soc.*, xxix., 156) that α-hydroxy-acids, in aqueous solution, yield α-ketonic aldehydes. Lactic acid, for example, gave methylglyoxal. It is now found that α-amino-acids behave similarly. Thus alanine, on digestion at low temperatures in faintly acid solution, with *p*-nitrophenylhydrazine may yield methylglyoxaldinitrophenylhydrazone. Other amino-acids, such as glycine, leucine, aspartic acid, phenyl-alanine, behave similarly. The yields are relatively small: $R{\cdot}CH(NH_2){\cdot}CO_2H \rightarrow R{\cdot}CO{\cdot}CHO + NH_3$.

The formation of α-ketonic aldehydes from α-amino-acids has interesting biological relations. It indicates, for example, a possible mechanism for the interconversion of alanine, lactic acid, and dextrose in the living cell, since each of these substances has been shown to be convertible into methylglyoxal, which in turn has been found by the authors to yield dextrose in the diabetic organism.

175. "*The Mode of Combustion of Carbon: the Effect of Drying the Oxygen.*" By Thomas Fred Eric Rhead and Richard Vernon Wheeler.

It was shown that the results of experiments with well-dried oxygen do not conflict with the supposition that, in the burning of carbon, a "physico chemical complex" is first formed, and that any carbon monoxide and carbon dioxide that may appear to be the primary products of combustion arise from the decomposition of this complex.

It would seem that decomposition of the complex is accelerated by the presence of moisture.

176. "*Cantharene, and Other Hydrocarbons Allied to the Terpenes.*" By Walter Norman Haworth.

An account was given of the synthesis of hydrocarbons of the dihydroxylene series, one of these being 1 : 2-*dimethyl*-Δ^2 : 6-cyclo*hexadiene*, $CMe\leqslant^{CMe:CH}_{CH\cdot CH_2}>CH_2$, the properties of which agree with those described by Piccard for the substance, cantharene, obtained from cantharidine by distillation with lime (*Ber.*, 1878, xi., 2122). The physical constants of this Δ^1 : 5-dihydro-*o*-xylene, and of a corresponding meta-derivative, were compared with the data recorded by Auwers for Δ^1 : 3 dihydro-*p* xylene, the gradation in the spectrochemical properties of the three hydrocarbons being analogous to that found for the three xylenes.

A lower homologue of the terpenes, C_9H_{14}, has also been synthesised, and its physical constants measured. This substance is 1-*methyl*-2-iso*propenyl*-Δ^1 cyclo*pentene*, $\begin{matrix}CH_2{\cdot}CMe\\ |\\ CH_2{\cdot}CH_2\end{matrix}\!\!>\!C{\cdot}CMe{:}CH_2$, and it differs in constitution from the terpenes only in respect of its containing a ring of five carbon atoms in place of the *cyclo*hexene structure of dipentene. The above hydrocarbon is the fourth member of the group of terpenes derived from *cyclo*-pentane, three others having been already described by Haworth and Perkin (*Trans.*, 1908, xciii., 573).

177. "*The Molecular Condition of Mixed Liquids.* Part I. *Mixtures of the Lower Aliphatic Alcohols with Water.*" By William Ringrose Gelston Atkins and Thomas Arthur Wallace.

From a study of the cryoscopic behaviour of mixtures of alcohols and water in aniline, no decided evidence could be obtained of any combination to form hydrates, even in the case of trimethylcarbinol, where the freezing-point concentration diagram shows the existence of a hydrate.

Mixtures of the alcohols and water in equimolecular proportions show a decrease in the contraction on mixing, when the alcohols are arranged in the same order as are their association factors, determined by Ramsay and Shields. Rise of temperature results in a decrease of the contraction on mixing in all cases except that of methyl alcohol, where, up to 43° at any rate, there is an increase of contraction. An explanation of this behaviour is offered in terms of the formation of hydrates. Calculation of the molecular volumes of these mixtures at various temperatures by means of Traube's constants points to the formation of hydrates containing equimolecular proportions of alcohol and water. These problems are being studied further.

178. "*The Purification of Acetone by means of Sodium Iodide.*" By Kathleen Shipsey and Emil Alphonse Werner.

It was recently shown (*Proc. Chem. Soc.*, xxix., 117) that sodium iodide can unite with acetone to form a crystalline compound having the composition $NaI,3C_3H_6O$. Experiments have now been made which show that acetone in a high degree of purity can be prepared from the commercial article in a very simple manner by the aid of sodium iodide. The hydrated salt $NaI,2H_2O$ may be used with advantage on account of its ready solubility in acetone; the solution when cooled to about −8° gives a very good yield of the above compound, and it is possible to obtain 70 per cent of the acetone in a pure state in a single operation. The purified acetone was found to be quite equal to that prepared by the rather tedious bisulphite process.

179. "*The Absorption Spectra of some Thio-derivatives of Benzene.*" By John Jacob Fox and Frank George Pope.

The absorption spectra of phenyl mercaptan and diphenyl sulphide were compared with those of phenol and diphenyl ether; and it was found that the substitution of sulphur for oxygen had resulted in an entire change in the character of both the vapour and solution spectra. The characteristic bands of the benzene spectrum were suppressed by the introduction of the thiol group into the molecule.

The spectrum of phenol vapour contained a large number of sharp narrow bands, which were absent from the spectrum of phenyl mercaptan. It was found that the position of the bands in the spectra of the solutions corresponded with certain groups of bands in the vapour state, and the extensions of the solution spectrum of diphenyl sulphide were definitely associated with the absorption bands in the spectrum of the vapour of this substance.

180. "*The Nickel Salts of the Benzildioximes.*" By Frederick William Atack.

It has been shown by Tschugaev that α-(*syn*)dioximes form nickel compounds, in which only one of the oxime groups has its hydrogen atom replaced by metal, but he has

repeatedly stated that both β-(*anti*-) and γ-(*amphi*-)dioximes do not yield nickel salts. It is now shown that γ-benzildioxime forms a definite and stable nickel compound in which both oxime groups are involved, giving a cyclic structure containing nickel. Tschugaev's statement that only α-dioximes are capable of forming nickel compounds is therefore untenable. All attempts to prepare a nickel compound of the β-modification have failed, nickel hydroxide being obtained in every case. It would appear probable from the results obtained that, of the oxime groups contained in 1 : 2-dioximes, in the α-(*syn*-) modification, one group is basic, the other acidic; in the β-(*anti*-) modification, both groups are basic, and in the γ-(*amphi*-) modification both groups are acidic.

181. "*Preparation of Seconaary and Tertiary Acid Amides from their Metallic Derivatives.*" By Jitendra Nath Rakshit.

When primary acid amides are heated with metallic sodium in indifferent solvents, they undergo condensation to secondary amides, which are isolated as sodium derivatives. Potassium under similar conditions gives, with formamide, potassium diformamide, but with acetamide and propionamide it yields only simple potassium substitution derivatives. From sodium diacetamide, di- and triacetamide are prepared by the action of hydrochloric acid and acetyl chloride respectively.

182. "*The Addition of Negative Radicles to Schiff's Bases.*" By Thomas Campbell James and Clifford William Judd.

The authors have investigated the formation and decompositions of a large number of the additive compounds formed from Schiff's bases with chlorine, bromine, iodine, and acyl haloids. In every case investigated, chlorine and bromine form dihalogen additive compounds, which are only sparingly soluble in non-ionising media, but dissolve readily (with partial decomposition) in alcohol, acetone, or ether. On treatment with water, acids, or alkalis, they undergo decomposition in two ways, (*a*) as indicated by Hantzsch (*Ber.*, 1890, xxiii., 2773) in the equation—

$$CHPh{:}NPh,Br_2 + H_2O = Ph{\cdot}CHO + C_6H_4Br{\cdot}NH_2(1:4) + HBr,$$

and (*b*) with elimination of halogen and production of the decomposition products of the Schiff's base. Alkalis favour the former, acids the latter decomposition.

The additive compounds with acyl haloids are of similar type, and are decomposed by warming with acids into aldehyde and acylamine.

With Schiff's bases iodine forms periodides, which, on heating gently, form red di-iodides.

The compounds may probably be formulated as quinquivalent nitrogen derivatives, although the possibility of a quinonoid structure is not entirely eliminated.

183. "*The Preparation of some Organo-selenium Compounds.*" (Preliminary Note). By Charles Weizmann and Henry Stephen.

The authors have prepared *selenodiphenylamine*, $C_6H_4<^{\text{-Se-}}_{\text{NH}}>C_6H_4$, which is obtained according to the two following methods :—(*a*) By boiling a mixture of diphenylamine and selenium in a metal-bath for thirty hours until the evolution of hydrogen selenide ceased; (*b*) by heating a mixture of the theoretical quantities of diphenylamine and selenium monochloride.

In both cases the product is separated from diphenylamine by distilling it under diminished pressure, and crystallising the crude substance from ethyl alcohol. Selenodiphenylamine crystallises from ethyl alcohol in pale yellow plates, which melt and decompose at 189°. The crystals on exposure to air gradually darken to a green tinge, and in solution with concentrated sulphuric acid a violet coloration is produced. The research is being continued.

(To be continued).

NOTICES OF BOOKS.

Occurrence and Nature of Carbonised Material in Soils. By Oswald Schreiner and B. E. Brown. Washington: Government Printing Office. 1912.

In this bulletin the nature and origin of the black organic particles in soils are discussed. These black insoluble particles are to be found in soils of various characters coming from widely separated parts of the United States. All surface soils contain them, and they are also present, though apparently to a slighter extent, in sub-soils as well as in specimens obtained from depths of from 15 to 50 feet. Various suggestions may be made as to their origin, and apparently no single explanation is always applicable. Agencies which may account for their occurrence are fire and deposition after erosion, and it is highly probable that, to a certain extent at any rate, they are the results of formative processes occurring in the soil.

Investigations of Methods of Analysis of Cane Products. By Wm. E. Cross. Louisiana: State University. 1912.

General methods of analysing sugar-cane products are shortly described and discussed in this bulletin, and some few modifications of some processes which are found tedious and slow in the sugar-works laboratory are suggested. Thus the author has worked out a slightly different method of determining sucrose in molasses, based upon the Clerget process, and he claims that it is both more convenient and more accurate. In some other minor points also he has modifications of prevailing methods to suggest, and his conclusions merit the attention of sugar-works' chemists.

CORRESPONDENCE.

DO UNUSUAL VALENCIES IN CERTAIN COMPOUNDS SOMETIMES CONNOTE GREAT STABILITY?

To the Editor of the Chemical News.

Sir,—May I call attention in your columns to the possibility that when unusual valencies are exercised in *certain* compounds great molecular stability may result, or be associated therewith. Nitric oxide (NO) and carbonic oxide (CO) are notoriously stable gaseous compounds, in which nitrogen and oxygen may be tetravalent, or carbon and nitrogen divalent. Carbon is, of course, normally tetravalent, at least such is the view held by many chemists. At any rate, the usual valencies attributed to some of the respective atoms are not apparently exercised in these compounds, and they are very stable gases.

Referring to Prof. Sir J. J. Thomson's X_3-gas of atomic or molecular weight 3, it will be apparent that, if this is a compound HH_2 or H_3, the usual valency of hydrogen is not exercised, at least in one atom, and a higher valency of, say, two becomes necessary. This body, according to Thomson's recent experiments, is exceedingly stable, being in many respects comparable with the inactive gases, helium, neon, argon, &c., but in mercury vapour it seems to combine or decompose (see report of the Bakerian lecture on "Positive Rays of Electricity," Chemical News, cvii., 271).

Is not this therefore an indication that X_3 *may after all be a polymeride of hydrogen?*

Another like element, however, mixed with neon in small relative quantities of atomic weight "22" was discovered, neon being regarded as a mixture of two inactive gases. So far as I know, this "element" has not been decomposed or combined in any way.

If X_3 turns out to be a definite element, like helium, even then it might be a polymeride of hydrogen, which

view, if true, would possibly reconcile conflicting deductions, a new conception of the term *element* then being necessary.

It is sometimes stated that of two different but plausible theories *both* cannot be right. We are only at the threshold of the temple of knowledge in these matters, and, when more is known, conflicting views may be reconciled with each other—to some extent at any rate.

Referring to an article of mine in the *Phys. Zeit.*, 1911, xii., 107), in particular to "Fig. 1" and "Fig. 2A," it will be seen that an inactive gas slightly below the atomic weight of helium (4) is diagrammatically indicated along with helium with an atomic weight of about 4. By continuing the secondary curve to zero origin in Fig. 2A, the values "22" (about) and "3" (about) would be intersected. These two values might appear to represent the gases discovered by Thomson, *but other higher values necessary to establish the secondary curve* (11) *are unknown.* A value of about 10 is also indicated in both of these diagrams, which value is common, like argon, to the two curves of Fig. 2A.

It is premature to come to any conclusion, but it is perhaps of interest to note these things while the problem awaiting further solution is fresh in the minds of many.—I am, &c.,

F. H. Loring.

"GENERAL INDEX."

To the Editor of the Chemical News.

Sir,—We have at the Laboratory a copy of your invaluable Index to your first 100 volumes, and I wish to make a suggestion about this, viz., that as perhaps most people have the bound volumes marked with the *year* only—and all your references are to the *volumes*, and properly so—that you have printed a slip giving in parallel columns volumes and year thus:—

Year.	Vols.
1860	1 and 2
1861	3 — 4

This could be gummed into the Index volume, and would be most valuable to the possessors of the "General Index."—I am, &c.

A. E. Johnson.

[We are having a slip printed in accordance with our correspondent's suggestion, and will be pleased to post a copy to all purchasers of the "General Index" who send us a request for the same, with their name and address in writing.—*Ed.* C.N.].

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Academie des Sciences. Vol. clvi., No. 13, March 31, 1913.

Compounds of Cerium Chloride with Gaseous Ammonia.—M. Barre.—Cerium chloride reacts with ammonia, the reaction being accompanied by the evolution of a fairly large amount of heat and a great increase in the volume of the mass. The compounds formed are all white powders, decomposable by water. Their formulæ are $CeCl_3.20NH_3$, $CeCl_3.12NH_3$, $CeCl_3.8NH_3$, $CeCl_3.4NH_3$, $CeCl_3.3NH_3$.

Determination of Calcium as Tungstate.—A. Saint-Sernin.—Calcium can be rapidly and accurately determined as tungstate, by precipitating a boiling ammoniacal solution of calcium chloride with an excess of a 20 per cent aqueous solution of neutral sodium tungstate. The heavy insoluble precipitate is filtered off, dried, and weighed, and its weight multiplied by 0·1944 gives that of the CaO.

Preparation of Primary Alcohols by Reduction of Ether Salts.—E. Chablay.—Primary alcohols can easily be prepared by reducing ether salts by means of sodammonium and alcohol. The reaction is—

$$R.COOR + 2C_2H_6O + 2N_2H_6Na_2 = R.CH_2.ONa + 2C_2H_5.ONa + 4NH_3.$$

From the ether salts of dibasic acids the di-primary glycols are obtained, both COOR′ groups being reduced.

Berichte der Deutschen Chemischen Gesellschaft. Vol. xlvi., No. 5, 1913.

Heat of Combustion of Diamond and Graphite.—W. A. Roth and H. Wallasch.—The authors have determined the heat of combustion of diamonds and of several kinds of natural and artificial graphite, using liquid paraffin to bring about combustion. The value they obtain for 1 gr. of diamond is 7869 cal., which agrees well with Berthelot and Petit's results. For graphite the mean value is 7854 gr. cal., while the French chemists obtained a higher value for graphite than for diamond.

Fluorides of the Noble Metals.—Otto Ruff.—It would be possible to prepare fluorine chemically if the fluorides of the noble metals could be obtained without using elementary fluorine. Attempts to convert gold and platinum chlorides into fluorides by means of anhydrous hydrofluoric acid or fused potassium difluoride were unsuccessful. It was found that Berzelius's "hydrofluosilicic acid platinum oxide" does not exist, for solutions of platinum dioxide containing very large quantities of hydrofluosilicic acid are hydrolysed, and on cautious evaporation leave platinum dioxide hydrate containing only small amounts of platinum silicofluoride. When a solution of potassium fluoride is added to a solution of platinum tetrachloride a precipitate is obtained which analysis shows to be the potassium salt of a pentachlorhydroplatinic acid. Osmium, ruthenium, and iridium react with elementary fluorine at a red heat to give fluorides. Rhodium and palladium are attacked only slowly.

Chemical Properties of Thorium C and Thorium D.—Walther Metzener.—There are two classes of reactions of short-lived radio elements, firstly those which occur in presence of an element chemically identical with them, and secondly those which occur in absence of such an element. Thorium C is inseparable from ordinary bismuth. It is usually separated by immersing nickel foil in a boiling hydrochloric acid solution of the active precipitate. The yield is very much lowered by the addition of a bismuth salt, but the thorium C is divided between the solution and the metal in exactly the same proportion as the bismuth. When the active precipitate is heated the thorium C begins to distil over at 700°. If the bismuth oxide containing thorium C is heated above its melting point no loss of thorium C occurs. An abnormal reaction of thorium C is its precipitation by silver haloid. This reaction does not occur in presence of bismuth. Thorium C crystallises with sublimate from a 15 per cent hydrochloric acid solution, and also with many tetravalent elements. It is tetra- or pentavalent in its crystallisation with niobium oxyfluoride-potassium fluoride. When thorium C is separated by nickel thorium D remains in solution. When a silver chloride precipitate containing thorium C is treated with ammonia the thorium D goes into solution while the thorium C is adsorbed as hydroxide by the filter. Thorium D agrees with thallium in its reactions and crystallises with thallium salts.

Action of Ozone on Liquid Ammonia.—W. Manchot.—When ozone is led into liquid ammonia at a low temperature the liquid turns a deep orange-red. The presence of a little water raises the temperature at which the phenomenon disappears. In anhydrous solvents saturated with ammonia the colour is not produced at a very low temperature, and organic amines do not give the reaction. The reaction occurs n presence of the least traces of ammonia.

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